SASKATCHEWAN RESEARCH COUNCIL

A SNOWPACK AND SURFACE WATER CHEMISTRY SURVEY OF SMALL LAKES IN NORTHERN SASKATCHEWAN

by

S.R. Shewchuk

SRC Technical Report No. 155

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INTRODUCTION

The chemistry of snowpacks has been used for many years to assess the impacts of natural and anthropogenic acid deposition. The monitoring of stable snowpacks for major ions and metals can give an excellent assessment of the impacts to be expected on the entire ecosystem.

Snow crystals are nucleated in the atmosphere by submicron size particles. Other particles can be collected by scavenging processes during crystal growth. Attachment of particulate impurities also takes place as the snow crystals move through the atmosphere during wet deposition. Between snowstorms dry atmospheric fallout and sources of contamination add to the impurities contained on the surface of the snowcover. All of these processes contribute to the chemical loading of a snowpack.

Soluble impurities in the snow are leached out very quickly with the first thawing of the snowpack. Thus a snowpack can store and suddenly release ions that can do considerable environmental damage. The process of impurity movement through snow has been described in detail by Colbeck (1981).

In addition, snowpacks collect atmospheric aerosols by having the particles fall into the snow crystal lattice and essentially become immobilized. The filtering effect of snow was described by Gjessing in 1977. As a result of surface winds the air volume within the snowpack is continually being replaced. The snow acts as a trapping medium for the particles moving with the winds. When all mechanisms are combined it turns out that a stable snowpack is an excellent collector of atmospheric aerosol particles and gases. Acidity profiles of ice cores taken from the Greenland ice sheet have revealed large volcanic eruptions in

the northern hemisphere during the past 10,000 years (Hammer et al, 1980). It is known that a history of air pollution chemistry is locked into the ice chemistry record of the northern regions. Acid concentrations in an ice core from Ellesmere Island representing the past 5,000 years of deposition were studied by Koerner at al, 1982. They were able to compare the snow chemistry of the earlier period with the past 25 years. Significantly higher concentrations of acid were deposited in the snow over the past 25 years at the same location.

The deposition of sulphate onto the snowpack of Norway has been studied by Johannessen and Hendricksen, 1978. Reported sulphate deposition ranged from 100 to 600 mg $(SO_4)/m^2$. Highest depositions occurred in the mountainous regions of the sea coast. Remote areas inland had deposition values less than 100 mg $(SO_4)/m^2$.

Most studies done on the snow chemistry of large continental land masses assume that if an element is distributed in the snow in a uniform way, then its origins are likely from natural sources. On the other hand, most metals and particulates emitted by industry are known to be alkaline and to fall out within 50 km of the source (Barrie, 1980).

Samples of snow from a wilderness area in New York State were analysed for inorganic ions (Galvin et al, 1978). Only nitrate and sulphate were found in large amounts. Typical values for nitrate ranged from 3.07 to 2.35 mg/L and for sulphate ranged from 3.44 to 1.88 mg/L. The pH values ranged from 4.2 to 5.6. In general the concentration of nitrate was larger than that of sulphate.

Snow chemistry of an area in northwestern Quebec has been studied

for major inorganic ion species (Frantisak et al, 1980). It is shown that the sulphate values are in the range of 0.48 to 1.76 mg/L and the nitrate values are in the range of 0.67 to 1.76 mg/L. The pH values range from 4.22 to 4.60. Virtually all of the free acidity can be accounted for by assuming that nitrogen and sulphur anions are the main source and origin of the hydrogen ion.

Over northern Saskatchewan a large portion of the yearly precipitation falls as snow. The pollutants contained in the precipitation accumulate in the snow to be released during short periods in spring. During a winter with little or no snowmelt before spring most of the pollutant load is retained in the snowpack. Accordingly, approximately 50-80% of the pollutant is released in the first 30 percent of meltwater (Johannessen et al, 1978). Accumulation in snow is a natural method to study air pollution deposition onto the area of Northern Saskatchewan.

Some studies (Shewchuk, 1979) have shown that trace levels of sulphur dioxide are entering the Precambrian region of Saskatchewan on an episodic basis. It is quite likely that this sulphur dioxide is combining with natural values and influencing acid deposition to some extent. However most studies reveal (Shewchuk, 1982) that current levels of acid deposition, especially during the winter months, are quite low.

It is thought that the pH of natural rainwater is controlled by dissolved carbon dioxide at a pH value of 5.6 and that decreases below this are due to the addition of acidic components by human activity. However there are many reasons for the decrease of pH below 5.6 due to natural sources. It is quite likely that the acidity of a rain or snow sample at any one location in space and time is a highly complex func-

tion of both natural and anthropogenic influences. Decreases could be due in part to naturally occurring acids from the air (Charlson et al, 1982). Even sulphur dioxide in trace amounts can dominate the carbon dioxide influences of acidity on precipitation. This is due to the fact that sulphuric acid is a strong, highly ionized acid, while carbonic acid is a weak acid. Other scientists (Chameides et al, 1983) have suggested that organic acids such as formic and acetic acid may well exert a significant control of precipitation acidity in remote areas. The sources of organic acids in the environment remain largely unknown. Since organic acids are not easily measured, it is difficult to quantify their role. The coincidence of low pH, high dissolved organic carbon and substantial anion deficit is usually taken as evidence of the presence of organic acids.

Global precipitation chemistry has been collected and studied by event collection to determine the composition and processes that control the chemistry. Ion balances have shown there are consistent anion deficits in some areas. Evidence such as this suggests (Keene, et al, 1983) that in some remote areas of the globe organic acids control the total acidity of precipitation. Organic acids contributed 64% of the acidity during the wet season at Katherine, Australia in 1981-82. The same researchers have done a field vs laboratory comparison of pH measurements (Keene et al, 1983), in almost every case it was shown that hydrogen ion was lost in transit between field and laboratory determination. Approximately 18% of the total acidity measured at field sites is lost. The loss is due either to the dissolution of calcium carbonate which would neutralize the acidity or initial organic acids that were measured

when the sample was first collected. The acidity was then consumed by microbes prior to analysis.

Reactive substances injected into atmosphere are either deposited as a gas phase or become integrated into airborne particles which subsequently are removed by dry or wet deposition processes. The pathway and rate of removal processes depend on physico-chemical properties which, in addition to the meteorological parameters, determine atmospheric residence time. It is with a knowledge of residence time that various types of atmospheric aerosols can be modeled. The residence time of particles for example is much shorter than for gases. All differing atmospheric aerosols have their own residence time.

Snow was sampled in the Bergen region of Norway (Forland, 1975). Several compounds and elements were studied including sulphate, magnesium, calcium, zinc, pH and conductivity. The mean values of these parameters were: 0.93 mg/L for sulphate, 0.12 mg/L for magnesium, 0.81 mg/L for calcium, 0.02 mg/L for zinc, 5.91 for pH, and 21 μmhos/cm for conductivity. A series of air mass back trajectories that gave precipitation supported the assumption that anthropogenic sources in the British Isles contribute to high pollution content of the snow.

Metals in the snow pack of Antarctica were reported by Gjessing et al (1973). Metals such as calcium, zinc, lead, cadmium and copper had concentrations such as; 0.13 mg/L, 26.9 μg/L, 1.6 μg/L, 1.44 μg/L and 16.0 μg/L respectively. In this location it is reasonable to assume that most metal constituents originate from natural sources. In Antarctica no melting occurs. Such elements are locked into the snow lattice structure and represent a long term history of atmospheric aerosol concentrations.

Heavy metal particulates have been monitored in the snow around many of the western Canadian smelters. Hazra et al (1975) studied the distribution of arsenic in snow near the metal smelters at Yellowknife, NWT. Results of the arsenic deposition in the snow close to the smelter ranged from 0.03 to 11.4 mg/L. The Canadian drinking water suggested guideline is 0.05 mg/L (As). At a location 50 km northeast of the smelter the arsenic concentration was 0.033 mg/L and 15 km west of town the concentration was 0.32 mg/L. A subsequent study in 1978 (Edwards et al, 1979) has shown that concentrations were reduced to below the drinking water guideline due to efforts at emission control.

Atmospheric fall out in the vicinity of a base metal smelter at Flin Flon was monitored by winter snow samples collected from the surfaces of frozen lakes (Franzin, et al 1979). Sample correlation analysis showed that the smelter was a significant source of zinc, cadmium, lead, arsenic and copper in the precipitation (snow and rain). Zones of influences for many of these metals extend beyond 100 km from the smelter. The Federal government has suggested guidelines for drinking water concentration on many of these metals.

A sulphur dioxide and heavy metal emissions study was reported about the smelter at Thompson, Manitoba (Wotton et al, 1981). One aspect of this study was to monitor the deposition to the snow out to 66 km. Patterns of trends away from the smelter were evident for zinc, copper and nickel, while elements such as cadmium were close to the detection

level. The pH values of the snow melt water were determined in this network, however, no correlation with distance from the stack could be drawn. A great deal of variability was found in the pH measurements. The sulphate in snow range from a concentration of 0.59 mg (SO_4)/L to 5 mg(SO_4)/L.

Snow cores were collected in the Athabasca Oil Sands region of northeastern Alberta in 1981 (Murray, 1981). A radius of 25 km about the oil sands plants was used. The amounts of sulphate and nitrate deposited in the snow had increased from a previous study, due likely to the commissioning of a second oil sands plant in the region. The amount of insoluble metal particulates decreased from the previous study (Barrie et al, 1978) due to the increase of emission controls for particulates. The sulphate concentration in the snow ranged from 0.29 mg(SO_4)/L to 3.23 mg(SO_4)/L and the nitrate ranged from 0.06 mg$(NO_3$-N)/L to 0.20 mg$(NO_3$-N)/L. The pH values were extremely variable from 4.5 to 7.2.

The Saskatchewan Research Council undertook an acid deposition study of Northern Saskatchewan in 1982 (Shewchuk, 1982). Although the main priority of the program was inorganic ion deposition into the snowpack of the northern parts of the province, several core samples taken as far away as 30 km from the smelter at Flin Flon revealed high levels of copper, zinc and arsenic in the snow.

It is known that freshwater lakes in ecosystems that are lightly buffered are sensitive to acid deposition. There has been much documentation of severe biological consequences in lakes that have been gradually acidified (Harvey, 1979). Most major fish production lakes are quite large and fed by smaller headwater streams and small lakes.

Lake acidification begins initially with small lakes and water bodies of the drainage basin. This then feeds the acid substances into the larger water bodies. It is important to study the issue of lake acidification not on the major lakes but in the small lakes and streams. This study in addition to collecting snow for atmospheric depositional chemistry purposes also collected and analysed lake water from the small lakes which serve as sites for the snow quality study.

The possibility of water bodies in northern Saskatchewan being influenced by acid deposition has been addressed by Liaw and Atton (1981). Water quality was compiled for over 600 lakes in Saskatchewan. It provides background information needed for assessment of the potential of acid depositional problems. Waters were classified according to their TDS (total dissolved solids) and alkalinity. Northern Saskatchewan lakes on the Canadian Precambrian Shield have surface waters that indicate that they are highly sensitive to acidic fall out. However, at present most lakes in the highly sensitive areas remain generally uncontaminated.

The snowpack chemistry of the area of northern Saskatchewan was presented in a previous report (Shewchuk, 1982). The objectives of the present report are to augment previous snow and lake water studies and include the following:

a) Examine last years data to determine if it is typical on a statistical long term average.

b) Compare the acidic deposition on a lake surface with that of a land surface.

c) Investigate the reason for low pH's as determined in many snow samples.

d) Drill several cores through the ice of selected lakes and extract a water specimen for analysis.

e) Interpret the data to determine the origin of the constituents measured.

PROCEDURE

Small lakes were selected as sites for the snow and lake water chemistry study because they allow convenient access for light aircraft. The primary selection process used for the site was that it be representative of a specified region of the province and that it be small enough to minimize snowpack drifting. Usually lakes with a surface area under 1 km^2 satisfied this criteria. The field program took place between March 21-28, 1983. Lake water samples were taken at snow sampling sites. Thus the network was not set-up from a regional study of the lake water.

The regional network contains 27 sites (see Figure 1). This year two sites were selected in Alberta and two sites were selected in Manitoba. This was thought to be necessary in order to present a coherent data set for observation and interpretation purposes. Table 1 shows the individual sites by number (see Figure 1) and the name of the closest lake on a 1:500,000 aircraft quality map. Several of the chosen lake sites were not named. The procedure adopted was to assign a number to the lake and name the individual site by the closest lake. In this report lake descriptions are made in terms of the name of the closest lake and not the number.

A detailed series of sites was established about the Haultain lake site to determine the fullest extent of a comparison between deposition onto the snowpack of a lake surface and the deposition onto the snowpack of a land surface. The purpose of this was to show what influence the land based ecosystems contribute to the overall acid deposition.

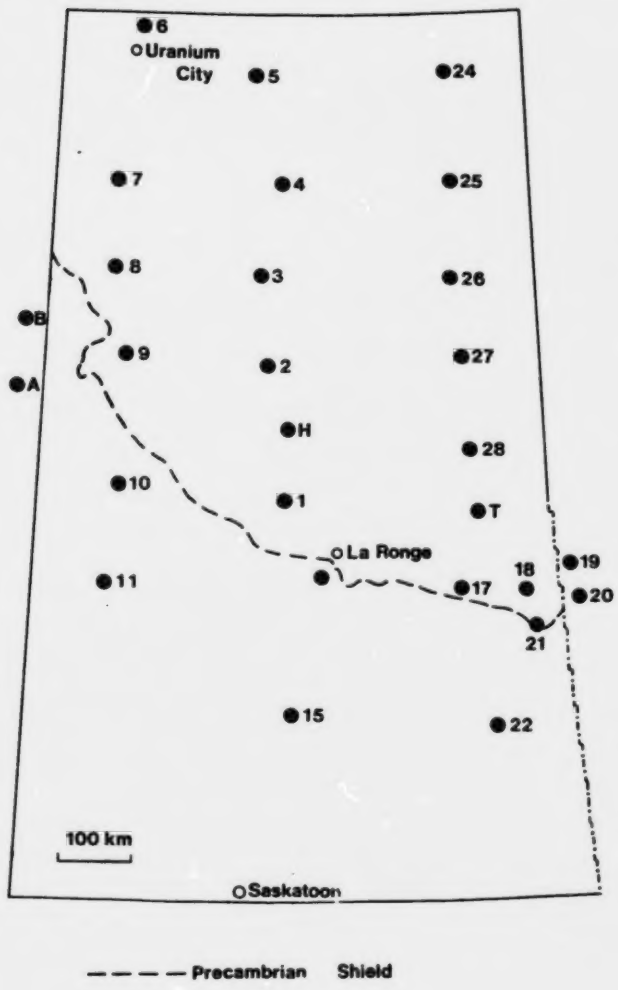


Figure 1. Regional site locations for snow and lake water chemistry study.

Figures 2 to 9 show the exact location of each small lake used as a site. Each figure is a sketch map of the individual site taken from 1:500,000 scale maps. These figures give an overall perspective as to just how the sites were located and to allow easy identification at some point in the future. Nearly all of these sites are highly remote and only available to aircraft access at this time. Lakes with minimum drifting were given high priority.

Normally the centroid of the lake surface proved to be the best location from which snow cores could be taken. A maximum of five snow cores were taken from each site, of which three would be analyzed chemically. The snow depth was measured for each core. Snow cores were taken with either a 10 cm or a 15 cm diameter acrylic tube 1.5 metres in length. Two diameter corers were used so that the snow volume could be controlled (i.e., for deep snow the smaller unit would be used and for shallow snow the larger diameter would be used). Normally the corer is inserted vertically into a clean, smooth area of snow. It is pushed through the snowpack to the ice surface. It is then dug out with a plastic shovel. The texture of the ice surface was noted carefully and if any slush or melting was detected the snow core was terminated just above the slushy area. It is important to bias the snow cores against slush and water present on some lakes because it is the chemistry of the snowpack that is the subject of this study and not the chemistry of a snow-water interface. The presence of melt-water on the ice surface below the snowpack was rare during this study. The ice surface at the base of the snowpack was usually hard, smooth ice.

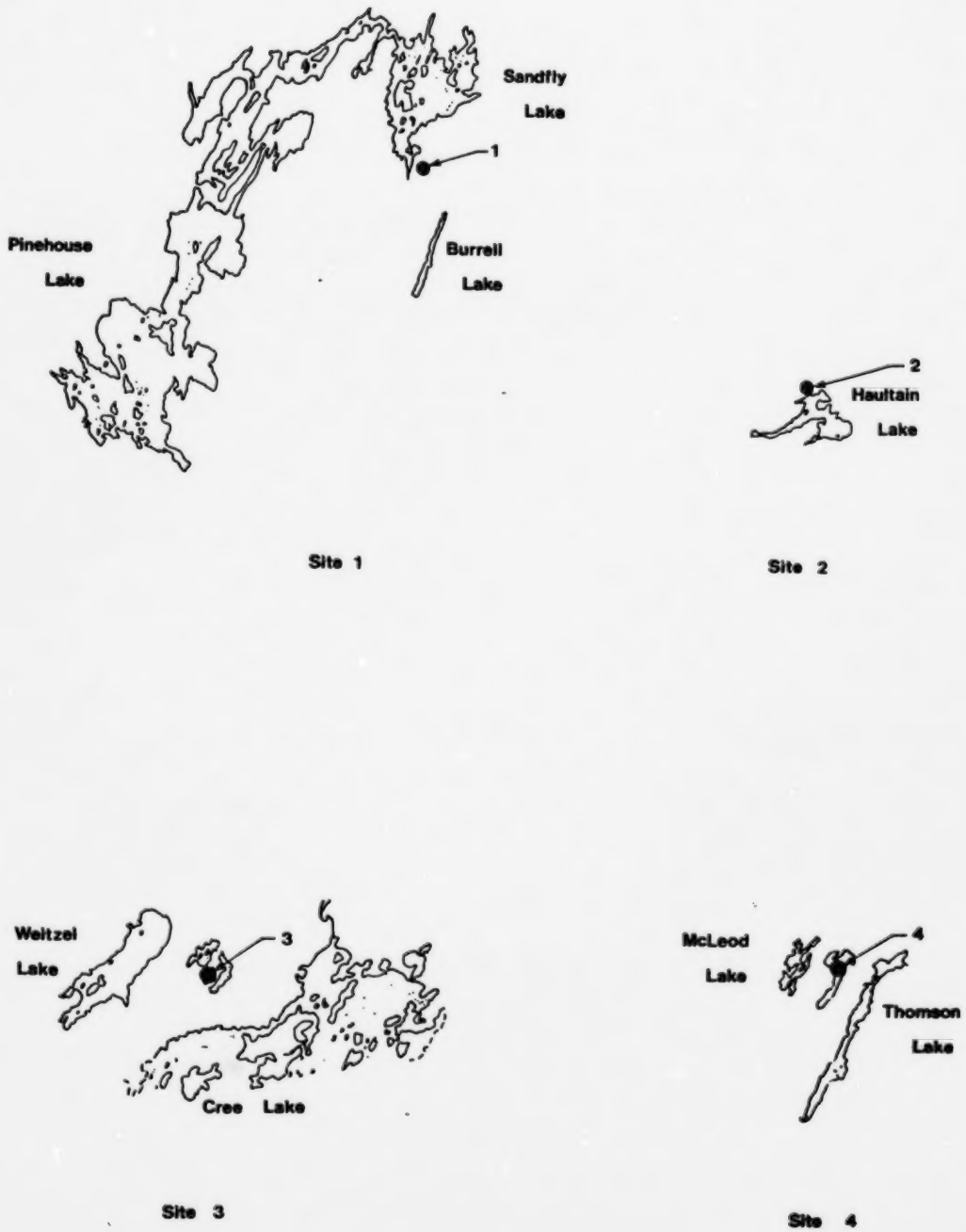
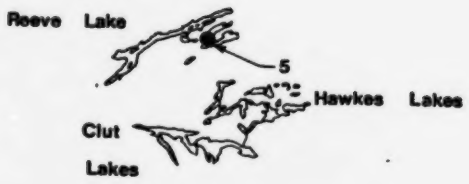
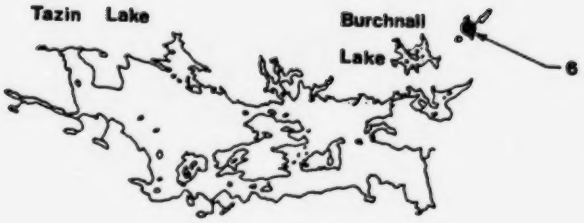


Figure 2. The location of lake sites 1, 2, 3 and 4.

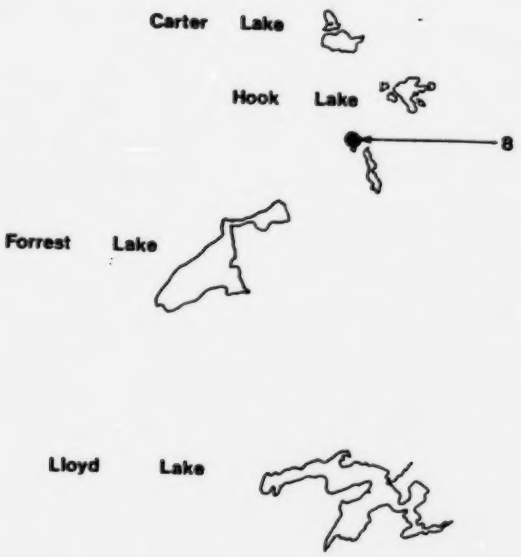


Site 5



Site 6

Site 7



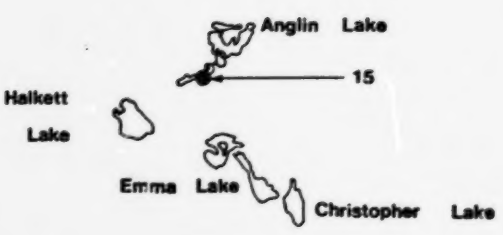
Site 8

Figure 3. The location of lake sites 5, 6, 7 and 8.

Site 9

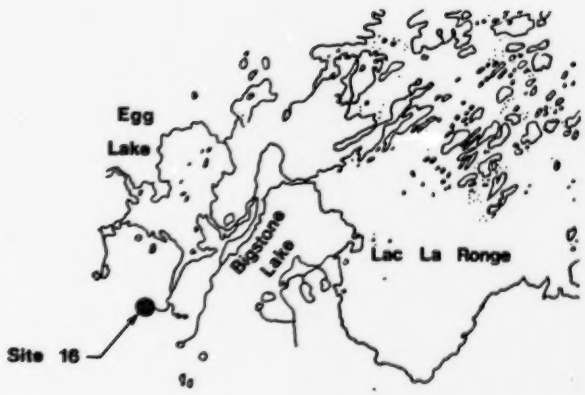
Site 10

Site 11



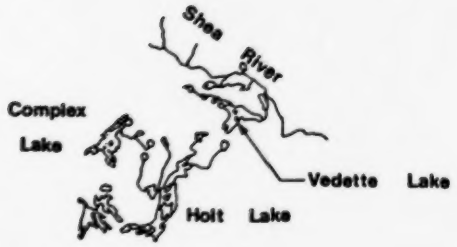
Site 15

Figure 4. The location of lake sites 9, 10, 11 and 15.



Site 16

Site 22



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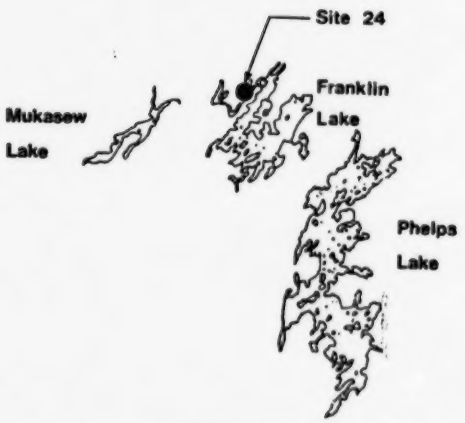


Site 24

Figure 5. The location of lake sites 16, 22, Holt and 24.

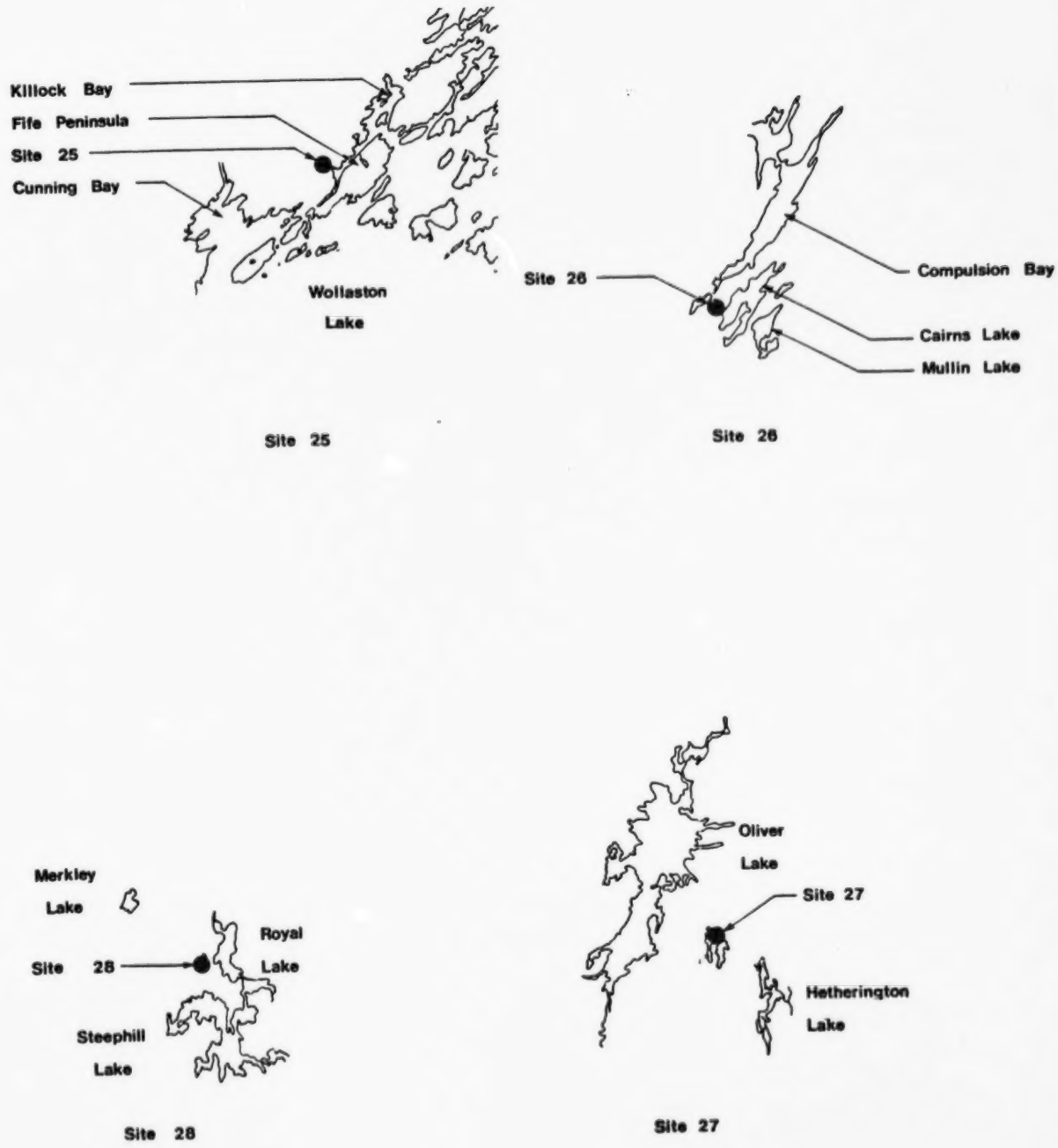


Figure 6. The location of lake sites 25, 26, 28 and 27.

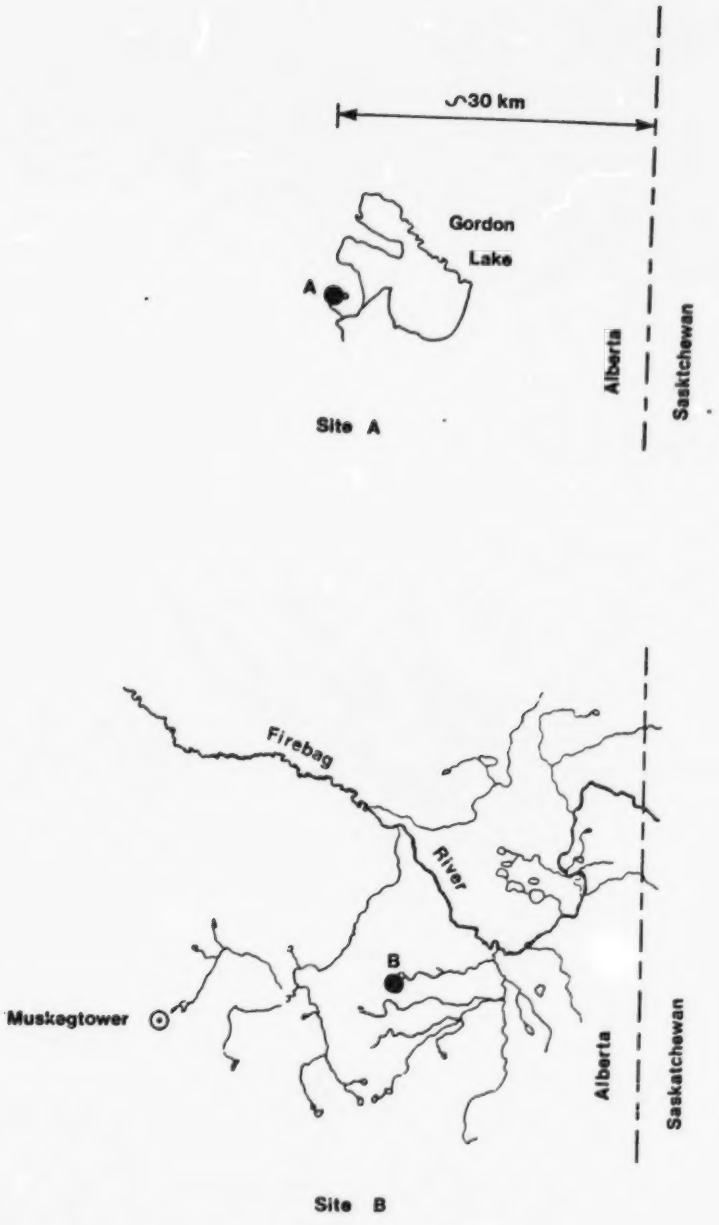
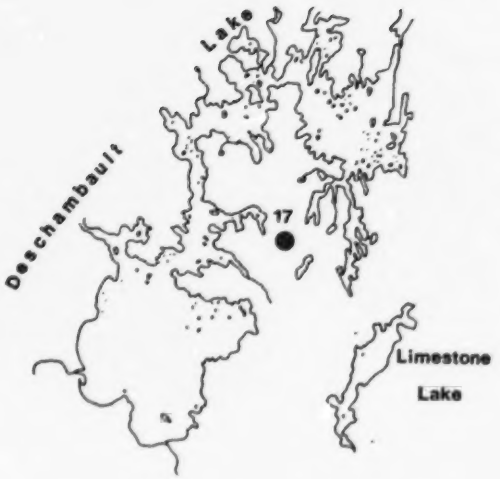
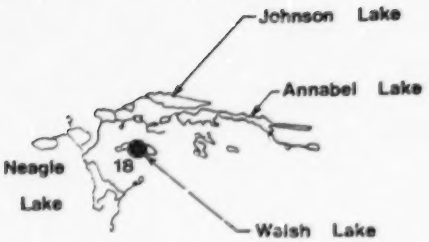


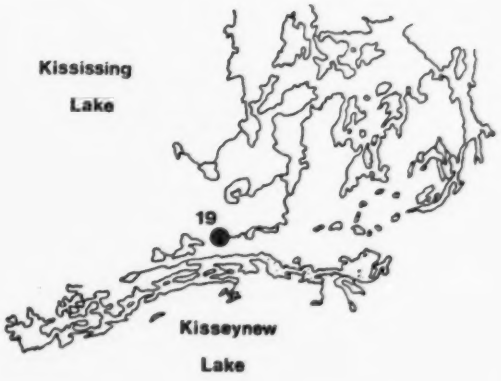
Figure 7. The location of lake sites A and B.



Site 17



Site 18



Site 19

Site 20

Figure 8. The location of lake sites 17, 18, 19 and 20.

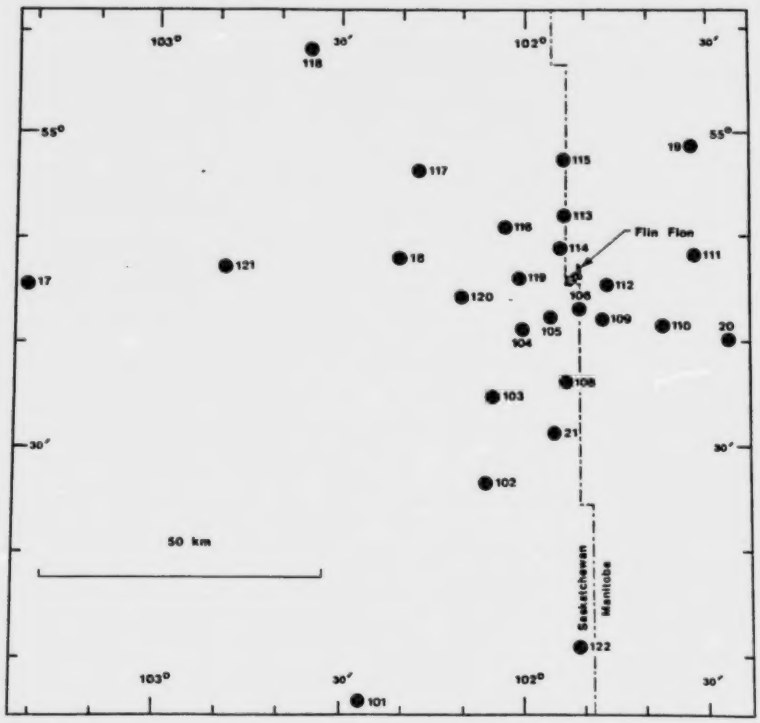


Figure 9. The local network sites for the snow studies about Flin Flon.

Once the snow core was collected within the corer it was placed in a pre-cleaned plastic bag, labeled and fastened with a zip-tie. The samples were then transported back to Saskatoon in a frozen state and remained frozen until the time of chemical analysis. As soon as they were melted, the sample volume, major ions and metals were determined.

To demonstrate the stability of the snowpack the maximum and minimum temperature structure for a number of locations within or near the study area was considered. The departures of the above zero °C isotherm is of concern here. Significant departures above zero °C indicates that the snowpack is undergoing melting and that likely any chemical pollutant material trapped in the snowpack would be leached out.

Lake water samples were collected from the same area as the snow cores. The snowpack was cleared off the ice surface to an area of approximately 2 m^2. A 10 cm hole was drilled and the hole cleaned of ice chips. Then a series of laboratory and field samples were extracted. A 3 cm diameter suction pump was placed into the water to a depth such that a sample of water was extracted one metre below the ice surface. The water was pumped into three separate polyethylene plastic bottles. One bottle (0.8 litres) was to be analysed for major ions. Another bottle (1 litre) was acidified with one percent nitric acid and analysed for metals. A final bottle (500 ml) was collected and treated with a 5 percent solution of potassium dichromate in a concentrated 12N solution of nitric acid and analysed specifically for mercury. The mercury in lake water was determined only at a few special sites. The main objective of studying lake water chemistry was to determine the nature and regional distribution of major inorganic ions.

Once the laboratory samples were extracted a series of field measurements was undertaken to determine: pH, conductivity, temperature and dissolved oxygen. All measurements were taken one metre below the ice surface. The field instrumentation was:

a) YSI Model 54A Oxygen Meter

b) Conductivity Meter Model 1484-10 Horizon Ecology Co.

c) Fisher pH/temperature meter 119.

It is most noteworthy that the selection of the network sites was based solely on criteria to determine the chemical species in the snowpack of the region. The lake water samples taken might not be typical of the water quality for the region.

In addition there was a smaller scale, local network set-up about the smelter at Flin Flon. The purpose of this network was to establish a series of 21 extra sites out to 100 km from the smelter. The primary siting criteria were similar to the regional study. However, the focus was on metals deposition to the snowpack from the smelter. Figure 9 shows the 26 lake locations of the area.

RESULTS

Meteorology of the region

Meteorological observations of daily maximum and minimum temperatures and 24-hour precipitation are shown in Figures 10 to 12 for Cree Lake, Flin Flon, Collins Bay, Prince Albert and Uranium City. The fact that the temperature seldom went above the 0°C isotherm indicates the winter period was sufficiently cold so that a major snow melt did not occur. Consequently the snowpack of 1982-83 can be used for acid depositional chemistry studies. If major snowmelt periods had occurred the snowpack could not be used for an acid deposition study.

The prevailing wind directions and speeds for several areas in the north, on a monthly basis, are shown in Tables 1 to 3. In the 1982-83 season there is a greater persistence of winds from the south and east at Collins Bay than during the comparable period a year earlier. At La Ronge the winds were most easterly than during the previous year. From the normal wind patterns in Table 3 La Ronge has had more prevailing westerly winds.

At Meadow Lake the wind regimes for both years were from the west and southwesterly directions predominantly. This year was typical of normal conditions at both Fort McMurray and Uranium City with a rather high persistence of easterly winds. A greater persistence of northerly and westerly winds occurred at Flin Flon during the 1982-83 period. This is typical of normal wind patterns. However in the 1981-82 season there was a greater persistence of southerly winds. At Lynn Lake predominant wind directions were from a westerly direction and this is

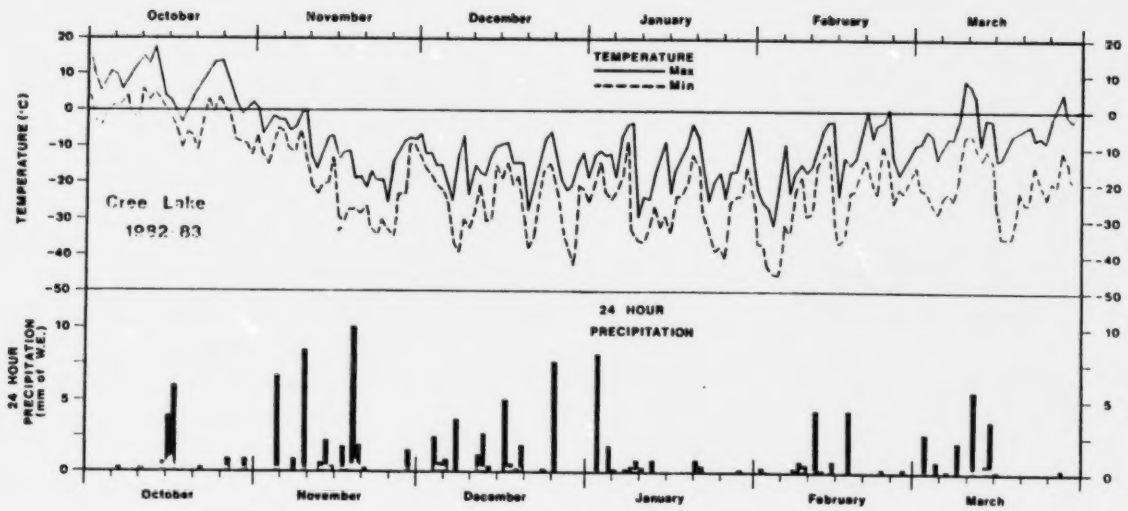
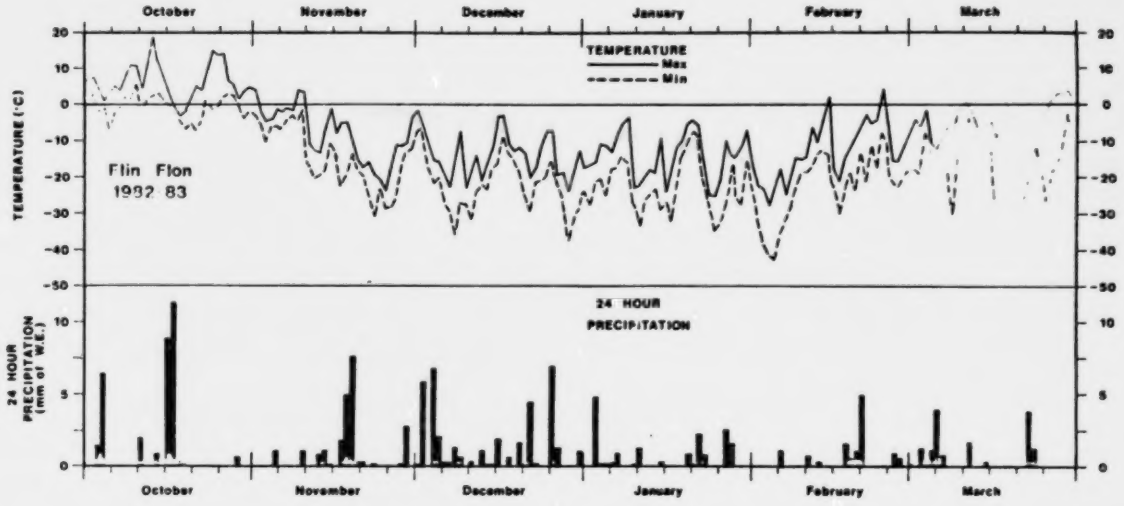


Figure 10. Temperature and precipitation for the Cree Lake area 1982-1983.



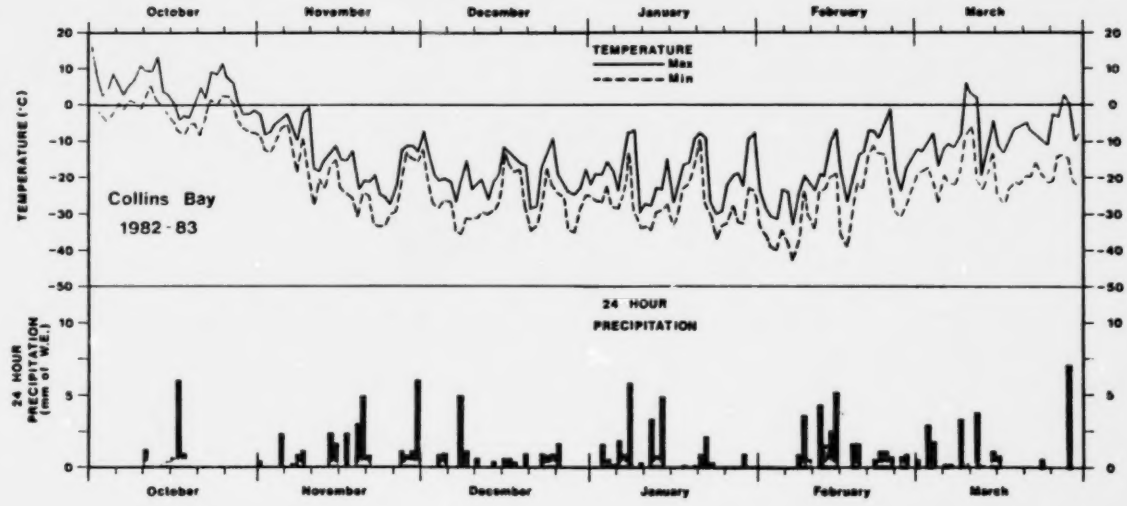


Figure 11. Temperature and precipitation for the Flin Flon and Collins Bay areas for 1982-83.

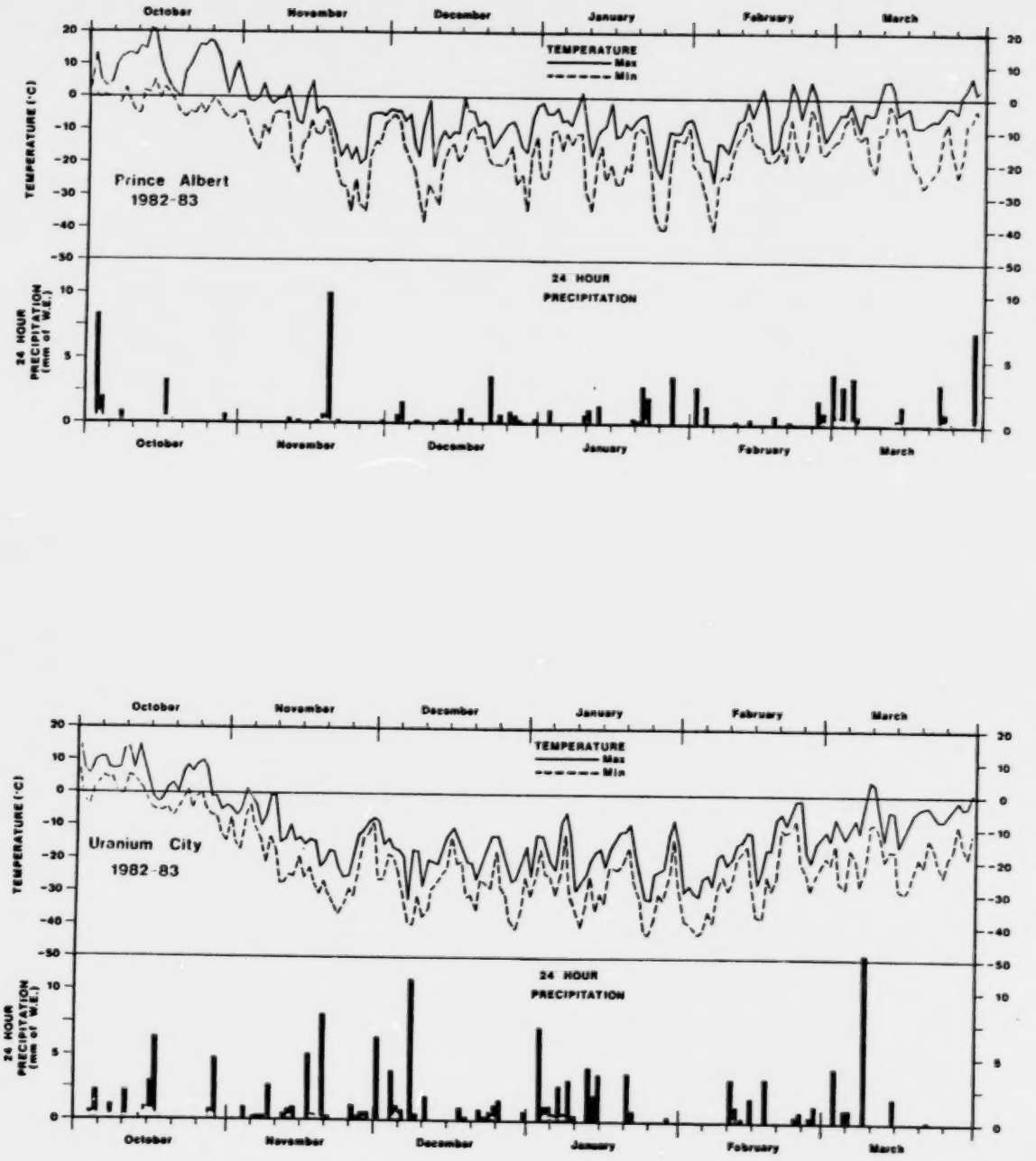


Figure 12. Temperature and precipitation for Prince Albert and Uranium City for 1982-83.

Table 1. Monthly mean wind speed and direction at centres within the study area 1982-83.

Location	1982 Nov.	Dec.	1983 Jan.	Feb	Mar
Collins Bay					
Prevailing Direction	WNW	WNW	S	S	SSE
Mean Speed (km/h)	11.6	9.3	14.6	14.0	14.0
La Ronge					
Prevailing Direction	W	ENE	W	ENE	S
Mean Speed (km/h)	12.4	10.0	9.5	9.6	9.6
Meadown Lake A					
Prevailing Direction	WSW	W	S	ENE	E
Mean Speed (km/h)	11.2	10.8	8.3	10.3	10.4
Fort McMurray A					
Prevailing Direction	E	E	E	E	E[a]
Mean Speed (km/h)	10.1	10.2	9.8	9.4	10.4[a]
Uranium City A					
Prevailing Direction	E	E	E	ENE	E
Mean Speed (km/h)	10.3	8.5	7.8	10.8	9.2
Flin Flon A					
Prevailing Direction	NNW	NW		NE	NE
Mean Speed (km/h)	12.3	6.6	N/A	7.1	6.8
Lynn Lake A					
Prevailing Direction	NNW	WNW	WNW	NNW	E
Mean Speed (km/h)	11.5	10.8	12.2	10.5	9.4

[a]Data is missing from the 5 - 17th inclusive.

Table 2. Monthly mean wind speed and direction at centres within the study area, 1981-82.

Station	1981 Nov.	Dec.	1982 Jan.	Feb.	Mar.
Collins Bay A					
Prevailing Direction	S	W	WNW	WNW	W
Mean Speed (km/h)	13.0	13.0	13.3	17.7	13.6
La Ronge A					
Prevailing Direction	S	W	W	W	W
Mean Speed (km/h)	10.7	9.8	9.5	13.1	11.1
Meadown Lake A					
Prevailing Direction	SW	W	SW	SW	SW
Mean Speed (km/h)	11.1	11.6	9.7	11.7	12.0
Uranium City A					
Prevailing Direction	E	E	ENE	W	ENE
Mean Speed (km/h)	10.0	9.3	7.2	8.7	9.2
Fort McMurray A					
Prevailing Direction	E	E	E	NW	NW
Mean Speed (km/h)	9.2	9.3	7.8	10.4	10.5
Flin Flon A					
Prevailing Direction	S	W	WNW	W	S
Mean Speed (km/h)	13.0	8.2	8.6	10.9	8.7
Lynn Lake A					
Prevailing Direction	S	W	NW	WNW	W
Mean Speed (km/h)	9.3	8.7	12.2	14.0	13.5

Table 3. Canadian climate normals (1951-80) wind direction and speed.

Location	Nov.	Dec.	Jan.	Feb.	Mar.
Collins Bay					
Prevailing Direction	S	W	W	S	S
Mean Speed (km/h)	13.1	12.4	12.1	12.8	13.2
La Ronge					
Prevailing Direction	W	W	W	W	W
Mean Speed (km/h)	9.9	9.0	7.9	8.8	9.4
Meadown Lake A					
Prevailing Direction	SW	SW	W	SW	SW
Mean Speed (km/h)	8.7	7.7	7.5	7.8	7.9
Fort McMurray					
Prevailing Direction	E	E	E	E	E
Mean Speed (km/h)	9.3	8.4	8.6	9.1	9.9
Uranium City A					
Prevailing Direction	E	ENE	ENE	ENE	ENE
Mean Speed (km/h)	11.6	9.2	8.6	9.2	10.9
Flin Flon A					
Prevailing Direction	NW	NW	NW	NW	NE
Mean Speed (km/h)	11.8	9.3	9.5	9.3	10.0
Lynn Lake A					
Prevailing Direction	W	W	W	W	E
Mean Speed (km/h)	12.4	11.3	13.2	12.0	12.2

Table 4. Monthly snowfall (cm) for the region for the 1981-82 and 1982-83 periods.

Station	1981 Nov.	Dec.	Jan.	1982 Feb.	Mar.	81-82 Total	1982 Nov.	Dec.	1983 Jan.	Feb.	Mar.	82-83 Total
Fort McMurray A	12.0	40.0	25.8	19.8	40.5	138.1	31.2	34.5	27.5	23.9	26.2	143.3
Collins Bay	26.7	32.2	7.4	15.0	22.4	103.7	35.2	26.4	47.2	48.8	40.8	198.4
La Ronge A	24.4	41.2	11.8	26.8	24.1	128.3	32.4	37.1	17.9	6.0	19.1	112.5
Meadow Lake A	7.6	26.5	9.7	12.3	14.4	70.5	20.5	9.6	17.6	13.6	11.6	72.9
Uranium City A	26.8	66.8	6.0	22.9	16.9	139.4	42.2	59.0	55.3	25.5	34.0	216.0
Flin Flon A	15.1	50.7	13.0	12.3	34.5	125.6	23.0	39.6	17.4	12.4	15.2	107.6
Lynn Lake A	32.1	11.2	9.6	22.6	8.7	84.2	35.6	54.4	29.1	18.2	20.2	157.5

typical of a normal wind pattern. All these wind observations were taken from the Canadian Climate Normals and the observations are the 10 metre wind direction and speeds. The amount of snowfall on the study area for the years of 1982-83 and 1981-82 is shown in Table 4. Significantly more snow fell in the 1982-83 season at locations such as Collins Bay, Uranium City and Lynn Lake, while areas such as Meadow Lake, La Ronge and Flin Flon received similar amounts in both years. The table does show that there is a large variability in snowfall to be expected in any one year in the northern area of the province.

Table 5 is a summary of the physical lake sites and the mean snow melt chemistry parameters. The lake sites were all tentatively assigned either a number or a letter. The mean snow depth that was observed on each lake is shown on this table. The standard deviation of 10 snow depths measurement is shown in brackets. It was quite difficult to select a site that had no drifting. The measurement was normally taken to the base of the ice surface. The chemistry parameters of: calcium (Ca), chlorine (Cl), bicarbonate (HCO_3), magnesium (Mg), sodium (Na), sulphate (SO_4), nitrate NO_3-N), ammonia (NH_3-N), conductivity and pH are all given as the mean value of usually three analysed cores. The mean value of pH was constructed by converting the pH value to hydrogen ion concentration. After averaging, this value is converted back to pH. The equivalent depth of water was constructed for each lake site by averaging the melt water volumes from each analysed core and dividing this value by the area of the corer. This value is an estimate of the vertical depth of water present in the corer.

Table 5. Mean values of snow melt chemistry parameters from the regional study.

Lake Number	Name of Nearest Lake	Snow* Depth	Ca (mg/L)	Cl (mg/L)	HCO_3 (mg/L)	Mg (mg/L)	Na (mg/L)	SO_4 (mg/L)	NO_3-N (mg/L)	NH_3-N (mg/L)	Cond. µmhos/cm	Equivalent Water Depth (cm)	Mean pH
1	S. of Sandfly	19(1)	< 0.05	< 0.08	< .5	0.02	<.1	0.94	0.14	0.05	6.7	3.85	4.85
2	N. of Haultain	28(3)	0.20	0.05	1.05	0.10	<.1	0.47	0.14	0.03	6.7	6.44	5.06
2(land)	N. of Haultain	48(7)	< .05	0.04	< .05	0.10	<.1	0.47	0.13	0.02	6.7	10.40	4.77
3	N. of Cree	22(3)	0.06	0.03	< .05	0.03	<.1	0.55	0.11	0.02	6.4	5.49	4.91
4	N. of Thompson	25(7)	< .05	0.02	< .05	0.02	<.1	0.52	0.10	0.03	6.0	5.97	5.10
5	N. of Hawkes	26(2)	0.28	0.06	1.17	0.07	<.1	0.51	0.10	0.04	6.0	5.13	5.00
6	N.E. of Tazin	33(1)	0.16	0.03	0.6	0.01	<.1	0.64	0.12	0.04	4.8	3.98	5.12
7	S.E. of Carswell	18(4)	0.09	0.05	< .5	0.04	0.2	0.65	0.12	0.04	8.0	4.40	4.77
8	S.W. of Hook	24(4)	0.24	0.03	0.06	0.07	<.1	0.89	0.15	0.06	6.5	5.19	5.25
9	N. of Wasekamia	22(1)	0.08	0.03	0.70	0.05	<.1	0.53	0.14	0.02	5.8	5.27	5.11
11	Lost	23(1)	0.21	0.11	0.90	0.08	<.1	0.54	0.12	0.04	5.1	5.93	4.92
15	Anglin	21(3)	0.29	0.05	2.17	0.42	.3	1.67	0.24	0.17	9.7	5.95	6.03
16	S. of Egg	19(2)	0.81	0.04	4.30	0.38	.2	0.57	0.16	0.15	4.0	3.90	5.41
H	Holt	23(1)	0.21	0.07	0.70	0.15	<.1	0.67	0.14	0.03	6.8	4.31	5.34
T	Tomahawk	31(3)	0.38	0.09	1.50	0.26	<.1	0.79	0.17	0.04	8.3	5.29	5.53
24	N. of Franklin	27(3)	0.13	0.00	0.83	0.07	<.1	0.57	0.10	0.05	5.5	5.02	5.45
25	N. of Wollaston	34(4)	0.06	0.06	0.20	0.021	<.1	0.51	0.08	0.02	5.3	6.94	4.99
26	N.W. of Cairns	25(5)	0.22	0.03	0.10	0.08	.17	0.73	0.15	0.04	7.7	4.93	5.05
27	E. of Oliver	31(5)	0.11	0.01	0	0.30	<.1	0.66	0.18	0.03	8.0	5.75	4.81
28	W. of Royal	27(2)	0.23	0.02	0.73	0.14	<.1	0.63	0.18	0.05	6.3	4.81	5.17
18	Welsh	31(2)	0.77	0.07	3.03	0.55	.2	1.93	0.22	0.08	12.3	5.12	6.94
17	E. of Deschambault	28(4)	0.47	0.06	1.6	0.22	<.1	1.07	0.21	0.12	8.0	6.04	5.97
21	N. of Nepe	30(2)	1.47	0.06	9.3	1.49	<.1	1.73	0.0	0.17	22.0	6.50	7.01
22	Kennedy	37(3)	0.06	0.40	0	0.03	<.1	0.60	0.22	0.10	8.7	7.36	4.89
A	S.W. of Gordon	22(3)	2.10	0.04	22.3	3.47	1.27	0.78	0.20	0.10	41.3	5.07	5.53
B	Muskeg Tower	25(3)	0.28	0.07	1.70	0.07	<.1	0.63	0.14	0.20	5.3	4.45	6.56
19	N. of Kisseynew	32(4)	0.12	0.00	0.6	0.10	<.1	0.59	0.18	0.08	6	4.57	5.49
20	N.E. of Payuk	32(3)	0.26	0.03	0.6	0.08	<.1	0.80	0.20	0.06	6	5.49	5.56

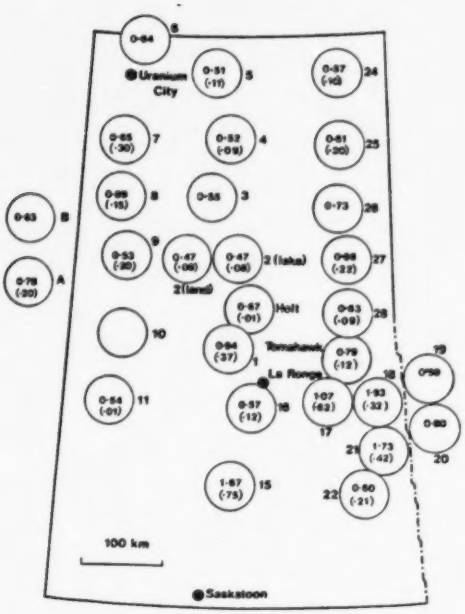
* The values in brackets are the standard deviation of measurements of snow depth taken at 10 locations from each site.

Snowpack chemistry

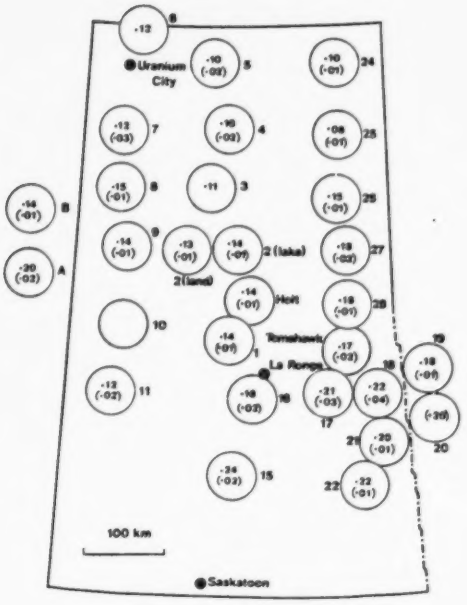
Table 5 shows that the major inorganic ions of bicarbonate, calcium, magnesium, sodium and chloride are primarily absent in the snow on the Precambrian Shield lakes. Anions such as sulphate and nitrate are present in lowconcentrations and they dominate the ion balance of the melt water solution by giving pH values that are in the range 4.8 to 5.5. Precambrian Shield lakes are lakes such as Sandfly, Haultain, Cree, Thompson, Hawkes, Tazin, Carswell, Hook, Wasekamio, Holt, Tomahawk, Franklin, Wollaston, Cairns, Oliver and Royal. Lakes that are located in shield transition zones and show slightly higher buffer capacity are: Lost, Anglin, Egg, Deschambault, Nepe, Kennedy, Gordon, Kisseynew and Payuk. These lakes in general have sufficient buffering capacity cations in the snow to maintain higher pH.

Figure 13 shows the spatial distribution of mean values of sulphate, nitrate, conductivity and pH in the regional study. The values in brackets represent the standard deviation of the series of individual cores at that site. The sulphate, nitrogen (as nitrate) and conductivity are reasonably uniform on the Precambrian Shield area of Saskatchewan. The concentration of all three parameters is higher in the southern area of the province and in the Flin Flon area. Most pH values on the Precambrian Shield are below 5.6. However, in the Flin Flon area and the Gordon Lake and Muskeg Tower areas of Alberta they are normally above 5.6.

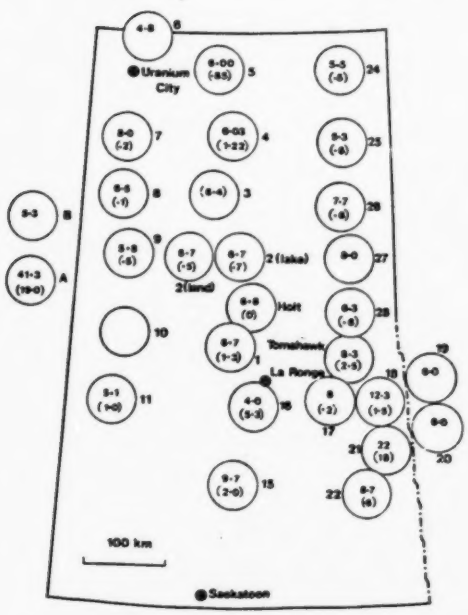
The sulphate variation on the Shield portion of Saskatchewan varies between 0.53 to 0.89 mg/L; the nitrogen as nitrate varies from 0.08 to 0.18 mg/L; the conductivity ranges from 4.8 to 8.0 µmhos/cm; and the mean pH variation on the Shield ranges from 4.77 to 5.46.



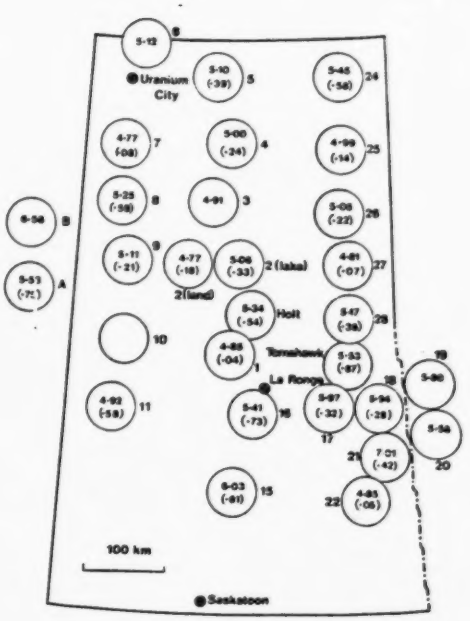
Mean Sulphate Concentration (mg/l)



Mean Nitrogen as Nitrate Concentration (mg/l)

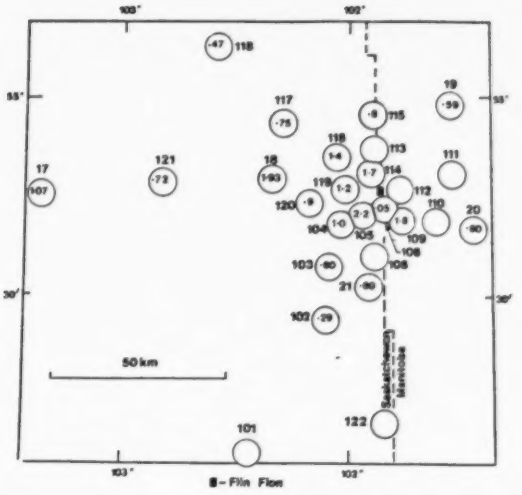


Mean Specific Conductivity (umho/cm)

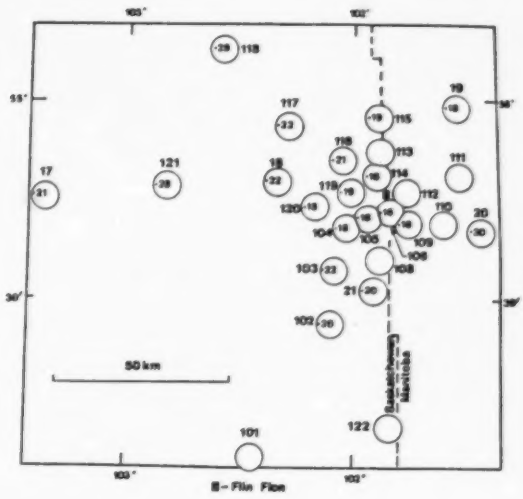


Mean pH Variation

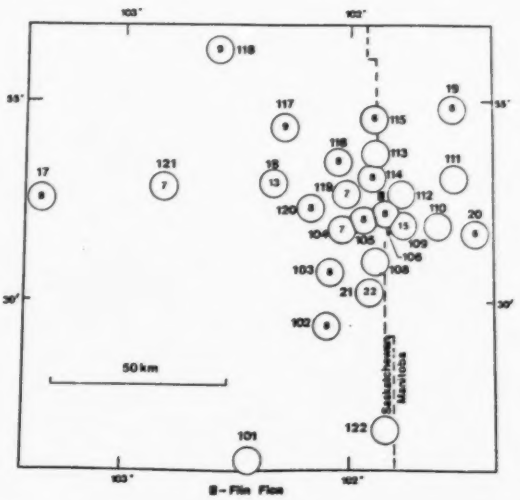
Figure 13. Mean values of sulphate, nitrate conductivity and pH in snow melt water collected in March 1983. Note the values in brackets represent standard deviations from the means at each lake site.



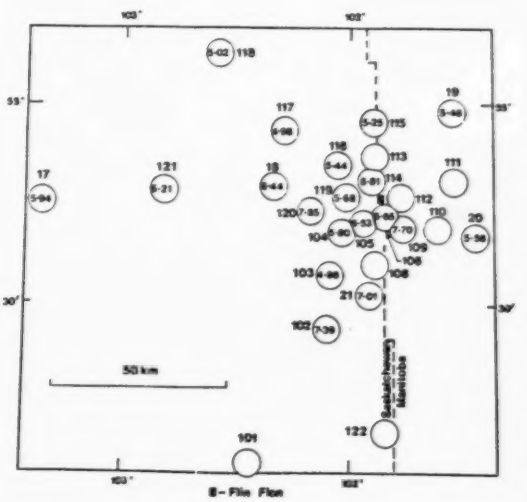
Sulphate Concentration (mg/L)



Nitrogen as Nitrate Concentration (mg/L)



Specific Conductivity (umho/cm)



pH Variation

Figure 14. The values of sulphate, nitrate, conductivity and pH in the snow melt water collected near Flin Flon in March 1983.

In the study about Flin Flon, the sulphate ranges from 0.05 to 2.2 mg/L; the nitrogen as nitrate ranges from 0.18 to 0.28 mg/L; the conductivity ranges from 8 to 22 μmho/cm; and the pH ranges from 4.98 to 7.85. There is an increase of sulphate; nitrate, conductivity and pH in the local study area as compared to the regional area. The spacial variation in this study is shown in Figure 14 for sulphate, nitrates, conductivity and pH. Detailed inorganic ion concentrations is shown in Appendix A. The names of the lakes sampled are given in Table 6. The sulphate distribution about Flin Flon was extremely variable. One site located on Potter Lake (106) showed sulphate of <0.05 mg/L, while the nearby site at Bootleg Lake (105) showed a maximum sulphate concentration of 2.2 mg/L. All of the values reported here represent one value of chemistry determination. As in most previous studies done about this smelter, the pH values were quite variable, ranging from 4.98 approximately 40 km northwest of the smelter to 7.70 southeast of the smelter at site 109. In general the pH values were significantly more on the alkaline side in this local network, as compared to the regional study.

Table 6. Site numbers and lake names in the local study about Flin Flon.

Lake Number	Name of Nearest Lake	Lake Number	Name of Nearest Lake
17	E. of Deschambault	110	E. of Athapapuskow
18	Welsh	111	Bryan
19	N. of Kisseynew	112	Manistikwan
20	N.E. of Payuk	113	S. of Oblong
21	N. of Nepe	114	Whitehead
101	W. of Cumberland	115	Haskin Bay
102	W. of Maraiche	116	Beatty
103	E. of Amisk	117	S. of Wildnest
104	Reynard	118	S. of Attitti
105	Bootleg	119	N. of Meridian
106	Potter	120	Magdalen
108	Byklum	121	N. of Hanson
109	Hook	122	S. of Namew

At the Haultain Lake site a series of 12 snow cores was taken from the land area and 4 cores from the lake area. The comparison of land-lake ion parameters is shown in Table 7. The means of 4 cores from the lake and 12 cores from the land surface are shown. The sites for these cores were uniformly selected from the four cardinal compass points about the lake so as not to bias the results to any specific corner of the lake-land structure. Within the limits of variability, sulphate concentration was quite uniform. There are slight decreases in nitrate, conductivity, snow density and pH as one moves from the lake to the land surfaces.

Table 7. Snow melt water chemistry parameters comparison between lake and land surface near Haultain Lake.

Surface	$SO_4^=$ (mg/L)	NO_3^--N (mg/L)	Conductivity (μmhos/cm)	Snow Density	pH (range)
Lake	0.47±0.06	0.15±0.01	6.9±0.6	0.23±0.04	4.81-6.75
Land	0.47±0.09	0.13±0.01	6.7±0.4	0.22±0.04	4.43-4.93

Table 8 shows the deposition of sulphate and nitrogen as nitrate in a vertical column of snow. The significant parameter in this comparison is the total deposition in a vertical column. Due to the fact that the snow depth is significantly larger on the land surface, the equivalent water depth is much larger. Therefore, the vertical deposition is much higher on the land surface. The deposition to lakes at other points within the regional study area is shown in Table 9. The majority of the area of the Precambrian Shield of Saskatchewan has sulphate depositions in the range of 27 to 33 $mg(SO_4)/m^2$. Sulphate deposition up to 100 $mg(SO_4)/m^2$ or more is present in the southern areas (Welsh Lake) and this is accompanied by an increase of pH.

Table 8. Deposition of sulphate and nitrate onto the snowpack on the lake and land surface of the site at Haultain Lake.

Surface	Depth (cm)	Melt Water (mL)	Equivalent Water Depth (cm)	Sulphate Deposition $(mg(SO_4)/m^2)$	(kg/ha)	Nitrate Deposition $(mg(SO_4)/m^2)$	(kg/ha)
Lake	28±4	529±62	6.5±0.7	30.6	0.31	9.8	0.10
Land	46±10	858±132	10.6±1.6	49.8	0.50	13.8	0.14

Table 9. Summary of sulphate and nitrate deposition onto a selected series of lakes in the regional study area.

Lake	Equivalent Water Depth (cm)	Sulphate Deposition $(mg(SO_4)/m^2)$	Nitrate Deposition $(mg(NO_3\text{-}N)/m2)$	pH (range)
Wasekamio	5.30	27.0	7.4	5.04-5.45
Carswell	4.40	28.6	6.2	4.69-4.82
Cairns	4.63	33.8	10.2	4.86-5.28
Royal	4.82	30.4	11.1	4.88-5.58
Welsh	5.41	110.9	35.7	6.72-6.93

A comparison of these major inorganic ion species with the previous year's work (Shewchuk, 1982) shows that sulphate and nitrogen as nitrate levels have increased at most locations in the north from previous years. In virtually every case the comparison of the exact physical site sampling point was similar in both years. Table 10 shows a comparison between the 1981-82 and the present study for the major parameters at the Haultain Lake site. Increases in the order of 10% or higher are evident for sulphate and nitrogen. The pH range is wider as well. The major parameter of interest in this comparison study is the total deposition of sulphate and nitrate into the vertical column of collected snow. The total sulphate deposition for this study was 30.6 $mg(SO_4)/m^2$ to the Haultain Lake area. The total nitrogen as nitrate was 9.8 $mg(NO_3\text{-}N)/m^2$. The previous year's results showed that 30.3 $mg(SO_4)/m^2$ and 6.5 $(NO_3\text{-}N)/m^2$ of sulphate and nitrate were deposited respectively. Within the limits of variability the total deposition to the snowpack is similar in each of the years.

Table 10. Comparison of snow melt water chemistry parameters for Haultain Lake between 1981-82 and 1982-83 results.

Year	$SO_4^=$ (mg/L)	NO_3^--N (mg/L)	Conductivity (µmhos/cm)	Snow Density	pH (range)
1983	0.47±0.06	0.15±0.01	6.9±0.6	0.23±0.04	4.81-6.75
1982	0.43±0.07	0.09±0.01	5.7±1.8	0.24±0.03	5.04-6.78

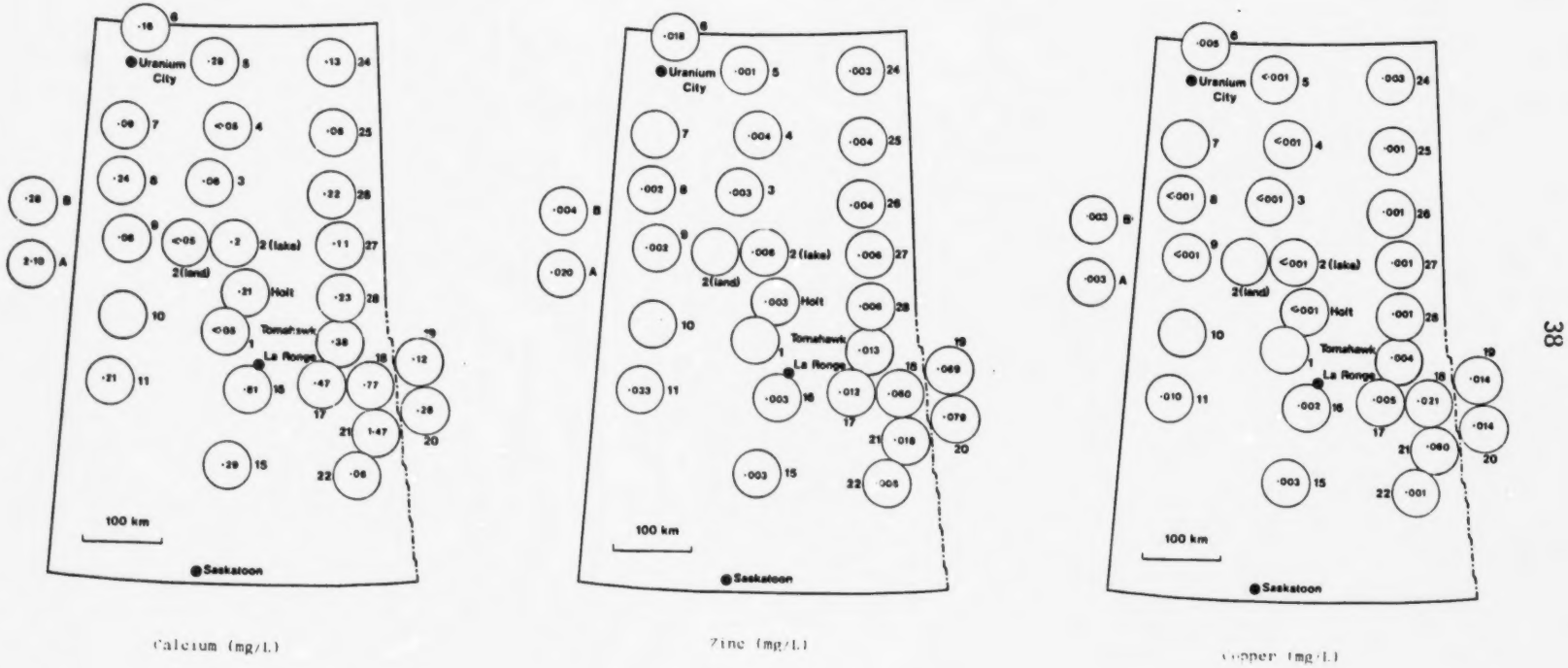


Figure 15. The regional distribution of calcium, zinc and copper in northern Saskatchewan snow March, 1983.

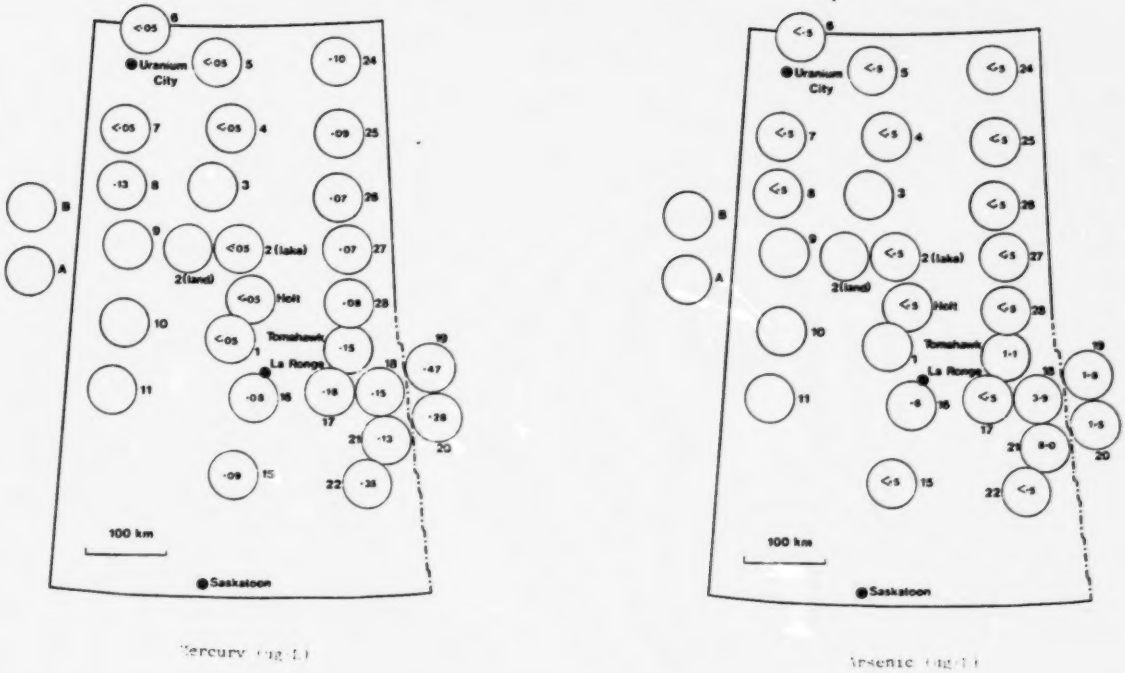
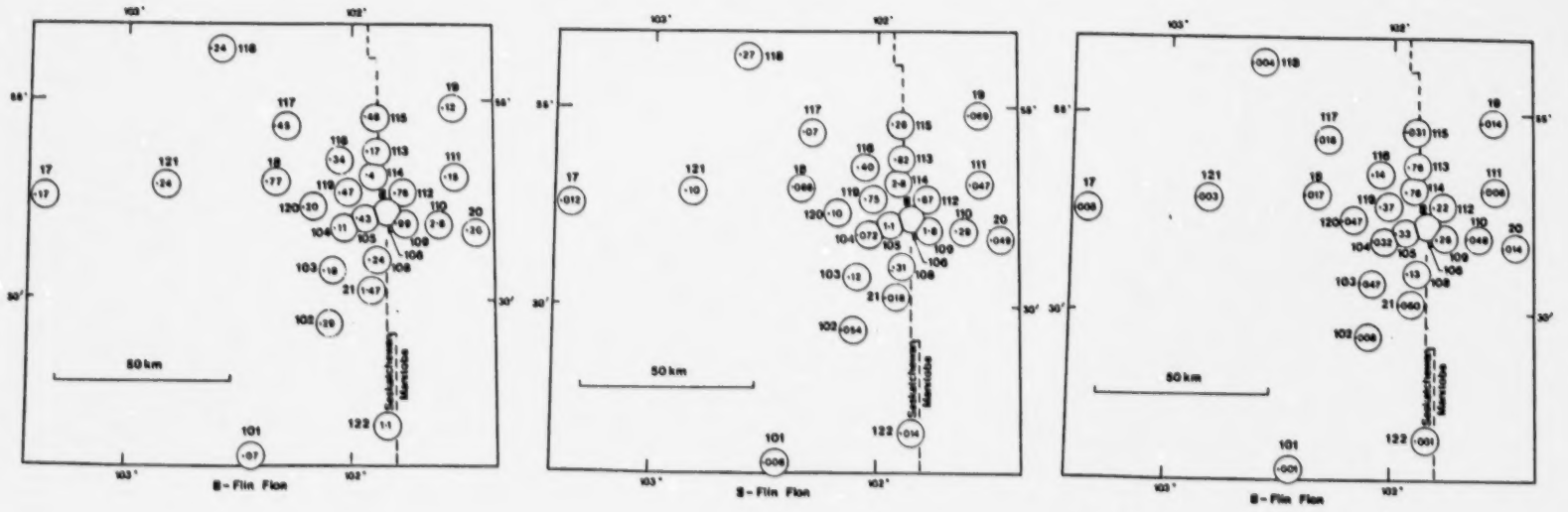


Figure 16. The regional distribution of mercury and arsenic in northern Saskatchewan snow in March, 1983.



Copper (mg/L)

Zinc (mg/L)

Calcium (mg/L)

Figure 17. The distribution of copper, zinc and calcium in the snow from the Flin Flon area March, 1983.

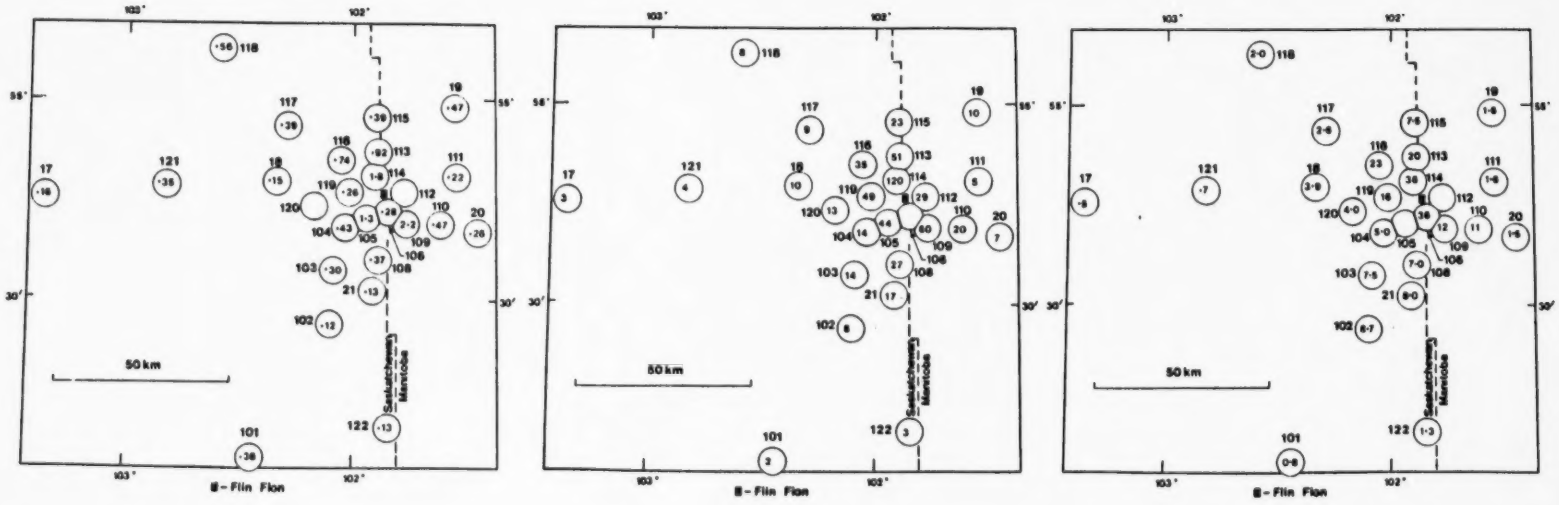


Figure 18. The distribution of mercury, lead and arsenic in the snow of the Flin Flon area March, 1983.

Metals in the melt water of the region study are shown in Figures 15 and 16. The metals shown are: calcium, zinc, copper, mercury and arsenic. Most metals clearly show a uniform distribution in the study area. However, there are local anomalies in the Flin Flon area for some of the metals. Figures 17 and 18 show a more detailed picture of the metals deposition about the Flin Flon area. The deposition of all metals shown here is higher as one approaches the smelter. Zinc at a maximum value of 2.8 mg/L is significantly above a background value of 0.006 mg/L. The influence of the smelter on the background zinc value extends well beyond 50 km from the smelter. There is a significant influence on background copper within 50 km. The natural background value of 0.004 mg/L is approached much more quickly. The background values for both zinc and copper were determined from the regional study. The values of 0.006 mg/L for zinc and 0.004 mg/L for copper were thought typical of the entire region of northern Saskatchewan. Low concentrations on a large area such as this indicate a natural background. Both arsenic and mercury can be transported long distances in the atmosphere. However the highest concentrations were observed within 20 km of the smelter. Both Tomahawk Lake and Holt Lake areas were included in this study because it is known that fish taken from these lakes have high levels of mercury in their tissue (Murray, A.R. 1980). Mercury levels were only marginally detectable at these sites.

Most of the lakes in the local study area show a measurable amount of mercury in the snow melt water with Haskin Bay (on Florence Lake), Whitehead Lake, Bootleg Lake and Hook Lake showing values that are above 1 µg/L of snowmelt water. Whitehead Lake and Potter Lake contained the

highest arsenic value observed at 36 µg/L. The values of lead are significantly above the background value of <.5 µg/L at several sites in the study area. The concentration of lead is near or above the value of 50 µg/L at Haskin Bay, Whitehead Lake, Meridian Lake, Bootleg Lake, and Hook Lake. The deposition of several metals onto the snow surface at several lakes within 50 km radius of Flin Flon is shown in Table 11. The elements of zinc and copper are shown at high deposition rates onto Haskin Bay, Whitehead, Beatty and Hook lakes. The zinc deposition is higher than the copper deposition by a factor varying from 3 to 8. The highest mercury deposition is shown at Hook and Whitehead lakes with the other lakes receiving approximately an order of magnitude less deposition. The deposition of arsenic and lead is highest at Whitehead, Beatty, Hook and Haskin Bay. In general, the area to the north and east of the smelter has significantly higher deposition. Arsenic, lead, and copper show regular decrease in depositional behavior away from the smelter.

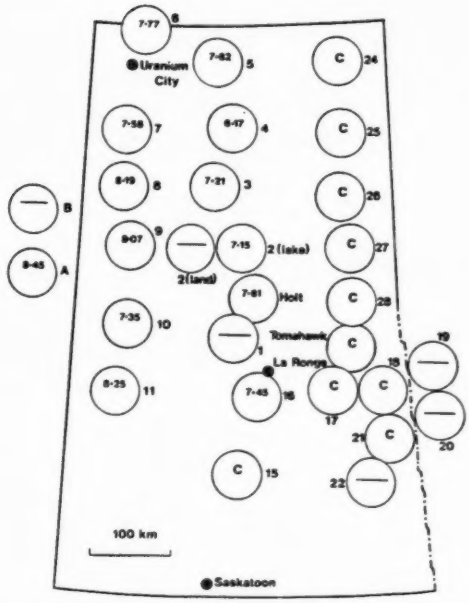
Table 11. Deposition of several metal elements onto a snow surface in the Flin Flon region.

Site	Deposition (mg/m^2) Zn	Cu	Hg	As	Pb
Welsh (18)	3.6	0.93	0.01	0.20	0.44
Haskin Bay (115)	17.7	2.0	0.02	0.41	1.45
Whitehead (114)	146.1	39.7	0.10	2.24	6.26
Beatty (116)	16.5	5.8	0.04	1.14	1.44
Hook (109)	98.8	14.3	0.13	0.72	3.29
Reyard (104)	5.7	2.6	0.01	0.29	1.12
Bryan (111)	2.8	0.4	0.01	0.11	0.30
Namew (122)	0.7	0.0	0.01	0.07	0.18
Holt (H)	0.2	0.0	0.00	0.00	0.10
Tomahawk (T)	0.8	0.2	0.01	0.05	0.30
Deschambault (17)	0.7	0.3	0.01	0.03	0.18

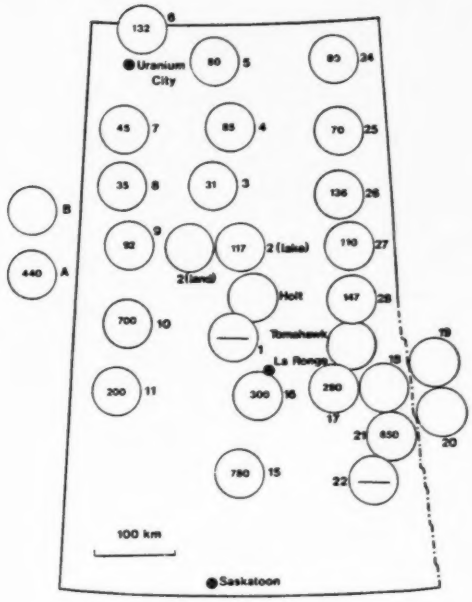
Lake water chemistry

The lake water survey was an important part of this program. The field measurements taken of the water quality parameters at the required sites are shown in Figures 19. At each site the instrumentation was fully calibrated in the field before a value was assigned. However at several lake sites the calibration was lost on the pH meter. Field measurements were taken at a depth of one metre below the ice surface. The lake water depth at each site was not measured. The site north of Thompson Lake is a muskeg swampy area. This was not realized until a hole was drilled through the ice and a strong odor was detected. A water sample was collected and analysed in the normal manner. The site was an anomaly as no other acid bog area was selected. Most pH readings are above 7.00 except the site north of Thompson Lake. Most field conductivity measurements were above 100 μmhos/cm at field temperature on either side of the province with the central part of the Precambrian Shield and the northeast sector of the province being an exception. In this area the conductivity was lower than 100 μmhos/cm. The one metre temperatures ranged from 1.0 to 3.0 °C with the Carswell-Cluff Lake area having the highest values. Dissolved oxygen levels ranged from 1.0 to 13.6 ppm. The values in most cases were quite erratic. Most of the readings however were considered to be low. This may have been due to the fact that a great many of the lake sites were small surface area water bodies and quite likely are very shallow. Hence the dissolved oxygen and other derived field readings could have been taken at or near the bottom of the water body.

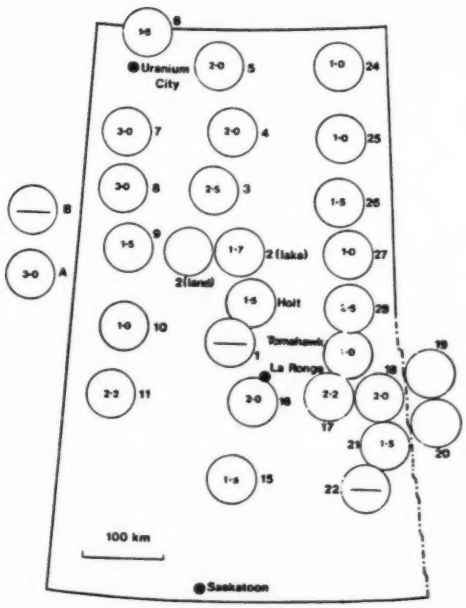
The results of the laboratory analysis of the lake chemistry study are shown in Appendix B. The values were determined analytically



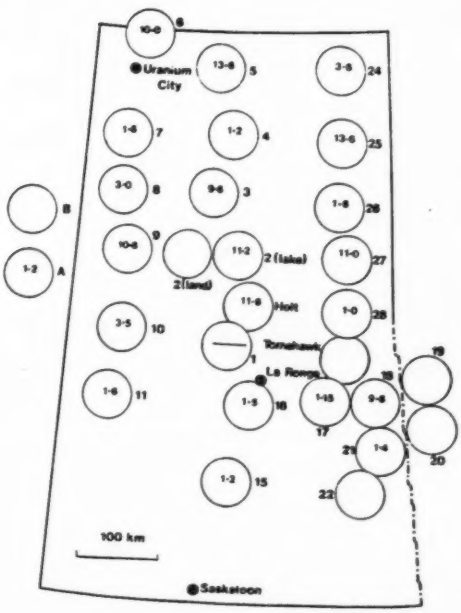
pH



Conductivity (umho/cm)



Surface Water Temperature (°C)



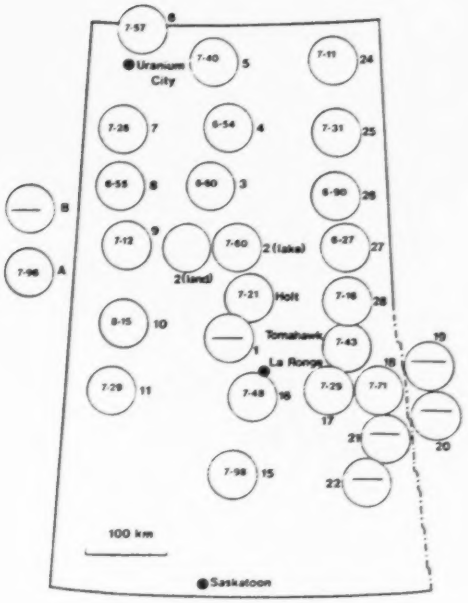
Dissolved Oxygen (ppm)

Figure 19. Lake water field measurements of pH, conductivity, surface water temperature and dissolved oxygen in northern Saskatchewan in March 1983. The value C represents no available data.

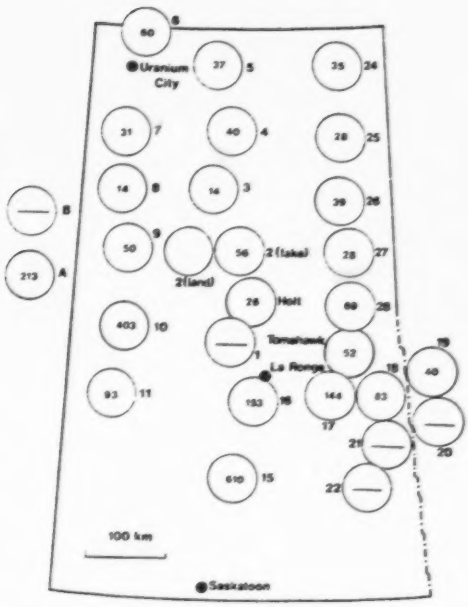
approximately two days after collection. The parameters measured in the lake water include:

- total suspended solids
- total dissolved solids
- conductivity
- pH
- alkalinity
- hardness
- total and orthophosphate
- total and organic carbon
- total nitrogen (kgedahal)
- nitrate (NO_3-N)
- ammonia (NH_3-N)
- chlorine (cl)
- sulphate (SO_4)
- calcium (Ca)
- potassium (k)
- sodium (Na)
- magnesium (Mg)
- iron (Fe)
- arsenic (As)
- mercury (Hg)
- selenium (Se)
- bicarbonate (HCO_3^-)

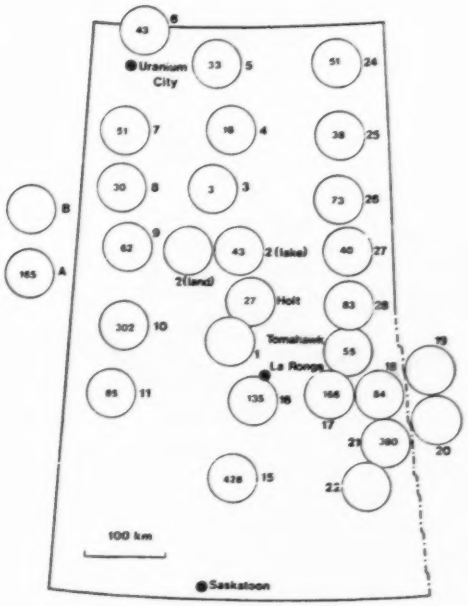
It should be noted that only one sample was collected on each lake. Therefore very little interpretation of the results is possible or attempted. Figure 20 shows some of these parameters plotted on a regional scale. The laboratory pH shows the same relative variation that was observed in the field data results. However the laboratory pH values all tend to be slightly lower. The conductivity values are quite comparable if the field measurements are normalized to 25°C. The TDS (total dissolved solids) and bicarbonate (HCO_3^-) values are quite variable throughout the region. TDS may be variable due to appreciable levels of suspended sediments because they are shallow lakes. However, the central area of Saskatchewan's Shield is quite low in both TDS and HCO_3^-. This confirms previous work on lake water sensitivities in the northern area of Saskatchewan. The lakes in the central Precambrian Shield are highly sensitive to acid deposition.



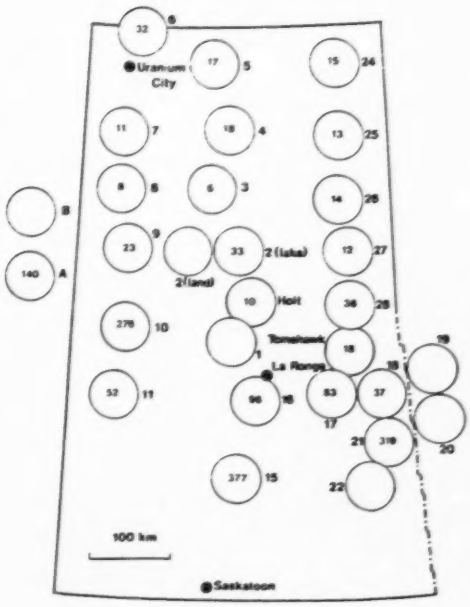
pH



Conductivity (umho/cm)



Total Dissolved Solids (TDS)



Bicarbonate Distribution

Figure 20. Lake water laboratory measured parameters of pH, conductivity, total dissolved solids and bicarbonate distributions for northern Saskatchewan waters in March, 1983.

DISCUSSION

Increases in some of the major ion concentrations were noted in this study in the Precambrian Shield snowpack. The area in the central portion of the Precambrian Shield lacks many of the buffering ions to modify the acid deposition. Whenever the major anions in the snow are sulphur and nitrogen, the pH values are consistently below 5.6. The ions of sulphur and nitrogen, while they remain at quite low levels as compared to the global context, still control to some extent the acidity of the snowpack. Any increases of sulphur dioxide or nitrogen oxides which deposit out over the Shield areas of the province will go directly into the unbuffered acid form. Areas that have high pH values such as the Alberta region (Gordon Lake and Muskeg Tower), the La Ronge-Anglin Lake area, or the Flin Flon area have sufficient buffering capability to absorb the present acid deposition flux.

Anthropogenic sulphur and nitrogen oxide is entering the Saskatchewan Precambrian Shield. Some of it is falling as an acid and contributing to the results of this study. It is not possible to access directly the magnitude of the impact due mainly to the lack of a stable series of baseline records. With a deposition to the snowpack on the Shield of under 100 $mg(SO_4)/m^2$, it is quite likely that natural processes are dominating. The high pH of the lakes (mostly >7.0) tend to confirm little ecosystem impact. There has been a regional increase of many parameters in this study over the previous year. However when the total deposition of sulphur and nitrogen to the snow core is examined it is seen that the real increases in total sulphur or nitrogen are quite small. The

important parameter in the acid deposition study onto the ecosystem is not the concentration of a particular species in the snow, but the absolute amount of that species in the vertical snow column (see Table 9).

Similar concentrations of sulphate and nitrate in the snow between the land and lake surface were observed in this study. It is evident that snow is drifting from the lake to the land surface but it is maintaining its chemical integrity. A large amount of the variability in deposition rates is due to the drifting of the snowpack. Estimating the amount of snow drifting off the lake is difficult.

There are consistently lower pH values of the snow in the land areas than on the lakes. Due to the large anion deficit at most locations it seems likely that organic acid particulates falling from tree branches to the snow may be having some effect (Keene et al, 1983).

There was a blow-out of a gas well in the early winter of 1982-83 in the Lodgepole area of Alberta, emitting 40 million CFD with a Hydrogen Sulfide content about 30% into the atmosphere (Lechner, 1983). It is possible that this emission source may have contributed to the increased depositions observed in the study. However, because other parameters such as nitrogen as nitrate were observed at higher values this year, it is likely that the Lodgepole emitter did not significantly affect this year's results.

Table 12 is a summary of the number of equivalents of sulphate and nitrogen as nitrate that are found in the snowpack of various areas of the world. Both of these ions can represent major sources of acidity for the snowpacks. In most areas where the sulphate and nitrogen is elevated the excess values are considered equivalent to a strong acid hydrogen ion concentration. The acidity of snow in Dorset, Ontario is

in the order of 3.9 (Martin, 1984). This is typical of areas that have hydrogen ion concentration in excess of 100 μeq/L in the snow and where acid deposition is a serious cause for concern. In contrast to this the sulphate and nitrogen concentration in northern Saskatchewan is comparable to that found in remote areas of the globe (approximately 20 μeq/L). The pH values of Antarctic snow is in the order of 6.7. This implies that there is some buffer ions present in the Antarctic, likely from the sea. The pH of Saskatchewan's snow is in the order of 4.9, implying that the sulphate and nitrogen as nitrate present are not buffered. At present there is a low level of acid deposition being received by the ecosystems of northern Saskatchewan's Precambrian Shield.

Table 12. Comparison table of sulphate and nitrogen (as nitrate) in the snow of several areas of the world.

Location	SO_4^{2-} (μeq/L)	NO_3-N (μeq/L)	References
Dorset, Ontario	50	63	CANSAP, 1982.
N.W. Quebec	18	46	Frantisak et al, 1980
Adirondacks	42	85	Galvin et al, 1978
Antarctic	10	8	Gjessing, 1973
N. Saskatchewan	9	10	present study.

The levels for most of the metals in the snowpack are near the global values as determined in remote areas of the globe. The Flin Flon smelter is the only source of zinc, arsenic, lead, mercury and copper in the area and the strong gradient away from the smelter indicates that it is the source of metal particulates in the snow. Sulphate and bicarbonate

concentrations also increase as the smelter is approached and acidity values decrease. Most local emitters are sources of particulates and these particulates are generally alkaline. On the other hand, gaseous emissions have a longer residence time and deposit as acids at some point farther away. Industrial particulate emission and natural particulate deposition likely cause the decreases in acidity of the snow near the smelter.

Holt Lake receives no flux of either mercury or arsenic in the snow. Tomahawk Lake, on the other hand, receives a low level of both mercury and arsenic in the snow. The value is only marginally detectable above background levels. There are many other lakes closer to the smelter that receive much higher fluxes. The presence of high mercury levels in fish in these lakes could be quite complex. There may be a relationship between the mercury in lake water, sediments or bedrock that is also a mechanism of contamination.

Table 13 is a summary of the amount of metal element mass deposited on the snow in the year 1977 and 1983 in the Flin Flon area. If it is assumed that the snow is a stable accumulator of metals, there is a decrease in the total metal accumulation on the lake surfaces in the most recent study. The decrease may be due to an increase in emission control effort by the smelter in the interim period.

Table 13. A comparison of the total mass of elements measured on Whitehead Lake and Hook Lake in 1977 and 1983 in kg.

Lake	Year	Zn (kg)	Cu (kg)	As (kg)	Pb (kg)	Reference
Whitehead (area 0.39 km^2)	1977	195	6.0	0.60	4.5	Frazin et al, 1979
	1983	57	15.5	0.87	2.4	Present study
Hook (area 0.90 km^2)	1977	950	24	2.7	24	Frazin et al, 1979
	1983	89	13	0.7	3	Present study

The lake water results have added to the data base of information from the northern Shield lakes. The results confirm that broad areas of the Precambrian Shield where the bicarbonate contents are low are highly sensitive to acid deposition.

RECOMMENDATIONS

1) It appears that useful information about the delivery of acids to ecologically sensitive areas by transport and transformation processes can be determined more quickly by direct empirical observations in the field than by any other means, such as extensive laboratory and modeling studies. Although the results of such field programs may not yield complete descriptions of all of the processes involved, the studies, if continued are likely to provide evidence with sufficient reliability to form a basis for improving the long term strategy for dealing with the problem of acid deposition in Saskatchewan.

Some of the important information will require at least 10 or 20 years of additional data collection to get a full understanding of atmospheric variability and atmospheric cycles. There are four sites within the area of Northern Saskatchewan where it is recommended that the study be continued on a long term basis. The Haultain Lake area is located on a productive portion of the Precambrian Shield. It has dense forest growth, and good fish populations. In addition there is a proven lack of buffering capacity in the precipitation and lake water. This area is a prime location for acid deposition studies. Other sites would be at the Carswell and Royal Lake areas. Carswell Lake is on the western part of the Precambrian Shield and Royal Lake is on the eastern portion near the sensitive Reindeer Lake complex. Another area that should be considered annually is the Welsh Lake area because sulphate deposition was several times higher than in the Precambrian Shield area. Metal deposition from the Flin Flon smelter has been confirmed in this lake.

It is recommended that a long-term snow survey network be established in northern Saskatchewan consisting of a minimum of four monitoring sites- Haultain Lake, Royal Lake, Carswell Lake and Welsh Lake. These areas should be monitored annually.

2) The chemical processing of sulphur dioxide and nitrogen oxide into acids by the atmosphere involves a multiplicity of chemical reactions. The relative importance of these various reactions changes significantly with time and location depending on the meteorological synoptic conditions. The deposition velocity of most anthropogenically orginating trace gases is much higher to rain water than to snow. This study has provided a good description of the deposition to the snowpack. In order to get a consistently coherent picture of the annual deposition it is recommended that regional deposition studies commence on the rain component. Saskatchewan Environment has in place an acceptable rain collection network. Data exists from this network for rain chemistry from major centres in the north. This data should be integrated with snow deposition data to arrive at a regional distribution of sulphate and nitrogen deposition to the sensitive areas of Saskatchewan on an annual basis.

It is recommended that acid deposition studies be undertaken to document total deposition to the ecosystems in sensitive areas of the province. Such studies involve rain and snow chemistry data.

3) While total deposition of most metals to the snowpack (for example zinc) is much less than in previous years, some metals such as copper, arsenic and lead are similar to depositions in previous years. The

smelter at Flin Flon is the most likely source of these metals. Because most metals have high fall velocities due to the fact that they are emitted into the air as particulates and not gases, their concentration is likely to be higher near the stack.

An area within 50 km of the stack will likely reveal the maximum possible concentration of these metals. It is recommended that research activities be consolidated into a series of long-term programs within this radius of Flin Flon. The long-term accumulation potential of deleterious impacts on lake water and lake sediments from most metals is not known at present.

It is recommended that a detailed metals study be done within 50 km of Flin Flon and long-term studies on metals deposition onto the ecosystems of the Flin Flon area be established.

4) Biological systems are extremely complex. The variable response of many of these systems in northern Saskatchewan to external stress will require long-term (decades) detailed study for evaluation. Any recommendations based on an imperfect data set are always incomplete. An increasing body of pertinent data whose quality and completeness can be expected to improve will be in place if sufficient research is established now.

Since small lakes are unlikely to be affected by acidic deposition at the present time, it is appropriate to begin major baseline studies of lake sediments, aquatic and vegetation inventories focussing on those species sensitive to acid deposition. There is a complex interaction between drainage basin, sediment composition and lake water that

must be considered. Also, the natural abundance of trace metals in lakes and sediments of the area has not been satisfactorily addressed at present. All of these studies should begin at some point if the effects of increasing acid deposition in northern Saskatchewan is to be completely understood. The areas of the province outlined in Recommendation Number 1 are suggested for this study.

It is recommended that long-term studies begin on biological systems of the area of northern Saskatchewan.

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APPENDIX A

Snow melt chemistry parameters

from the Flin Flon area

APPENDIX A: SNOW MELT CHEMISTRY PARAMETERS FROM THE FLIN FLON AREA

Lake Number	Name of Nearest Lake	Ca (mg/L)	Cl (mg/L)	HCO_3 (mg/L)	Mg (mg/L)	Na (mg/L)	SO_4 (mg/L)	NO_3-N (mg/L)	NH_3-N (mg/L)	Cond. (µmhos/cm)	pH
102	W. of Maraiche	0.50	0.058	3.7	0.47	<0.1	0.29	0.20	0.06	8	7.39
103	E. of Amisk	0.09	0.017	Nil	0.05	<0.1	0.60	0.22	0.04	8	4.86
104	Reynard	0.06	0.023	0.8	0.07	<0.1	1.0	0.18	0.32	7	5.80
105	Bootleg	0.41	0.02	1.4	0.10	<0.1	2.2	0.18	0.06	8	6.53
106	Potter	0.38	0.25	2.0	0.13	0.1	<0.05	0.16	0.06	8	6.65
109	Hook	1.5	0.085	6.5	0.41	0.1	1.8	0.16	0.04	15	7.70
114	Whitehead	0.14	0.037	1.2	0.05	<0.1	1.7	0.18	0.06	8	6.81
115	Haskin Bay	0.18	0.030	0.5	0.08	<0.1	0.80	0.19	0.05	6	5.25
116	Beatty	0.33	0.025	0.8	0.10	<0.1	1.4	0.21	0.08	8	5.44
117	S. of Wildnest	0.12	0.015	Nil	0.04	<0.1	0.75	0.22	0.07	9	4.98
118	S. of Attitti	0.23	0.016	Nil	0.08	<0.1	0.97	0.28	0.06	9	5.02
119	N. of Meridian	0.32	0.043	0.9	0.08	<0.1	1.2	0.19	0.06	7	5.68
120	Magdalen	0.45	0.047	2.5	0.34	0.2	0.90	0.18	0.07	8	7.85
121	N. of Hansen	0.23	0.012	0.5	0.08	<0.1	0.72	0.28	0.14	7	5.21

APPENDIX B

Water chemistry for small lakes in northern Saskatchewan

APPENDIX B: WATER CHEMISTRY FOR SMALL LAKES IN NORTHERN SASKATCHEWAN

Lake Number	Name of Nearest Lake	Ca (mg/L)	Cl (mg/L)	CO_3 (mg/L)	HCO_3 (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	SO_4 (mg/L)	T.Alk. (mg/L)	T.Hard (mg/L)	NO_3-N (mg/L)	NH_3-N (mg/L)	T.D.S. (mg/L)	T.S.S. (mg/L)	Cond. (µmho/cm)	pH
1	W. of Gordon	34	0.4	Nil	140	2.7	13	3.5	0.8	115	138	<0.005	0.15	165	10	2.13	7.96
2	N.W. of Haultain	5.7	0.3	Nil	33	0.6	3.6	1.4	1.1	27	29	0.03	0.10	43	3	56	7.60
3	N. of Cree	1.2	0.1	Nil	6	0.4	0.5	0.6	1.3	5	5	0.03	0.10	16	3	14	6.60
4	N. of Thompson	3.2	0.8	Nil	18	0.8	1.1	1.2	1.1	15	13	<0.005	0.36	39	16	40	6.54
5	N. of Stoney, S. of Reeve	4.9	0.2	Nil	17	0.7	1.4	0.8	2.6	14	18	0.03	0.04	33	2	37	7.40
6	N.E. of Tazin	10	0.8	Nil	32	0.6	1.7	1.7	1.6	26	32	0.03	0.10	43	2	60	7.57
7	S.E. of Carswell	2.6	1.2	Nil	11	0.5	0.9	1.1	1.4	9	11	<0.005	0.36	51	20	31	7.26
8	S.W. of Hook	2.1	0.4	Nil	8	0.3	0.4	0.7	1.3	7	7	0.20	0.42	30	2	19	6.55
9	N. of Waskamid	4.7	1.6	Nil	23	1.6	2.4	3.2	1.5	19	22	0.11	0.10	62	2	50	7.12
10	S.W. of Buffalo Narrows	35	1.0	Nil	276	9.6	33	21	0.5	226	223	<0.005	0.09	302	4	403	8.15
11	N.W. of Lost	13	0.2	Nil	52	1.2	5.4	1.5	2.2	43	54	0.42	0.04	85	2	93	7.29
15	Anglin Lake	68	1.6	Nil	377	4.3	42	18	46	309	342	0.06	0.25	428	1	610	7.98
16	S. of Egg	24	0.5	Nil	96	1.1	6.6	3.5	2.4	79	87	<0.005	0.98	135	34	153	7.48
17	E. of Deschambault	17	1.0	Nil	83	3.4	7.1	4.5	1.2	68	72	<0.005	0.50	166	12	144	7.29
18	W. of Flin Flon	9.8	0.7	Nil	37	1.0	4.0	1.9	8.0	30	41	0.09	0.08	84	2	83	7.71
21	W. of Athapapuskow	58	0.9	Nil	319	1.7	38	4.2	10	262	301	<0.005	1.0	380	12	482	8.24
24	N.W. of Franklin	3.0	0.2	Nil	18	0.4	1.4	1.0	1.5	12	13	<0.005	0.22	51	15	35	7.11
25	N. of Wollaston	2.5	0.5	Nil	13	0.5	1.1	1.2	2.5	10	11	0.005	0.06	38	1	28	7.31
26	W. of Cairns	3.6	0.4	Nil	14	1.0	1.5	1.8	2.9	12	15	<0.005	0.16	73	17	39	6.90
27	E. of Oliver	3.0	0.4	Nil	12	0.4	1.0	1.1	1.6	9.6	12	0.02	0.08	40	2	28	6.27
28	W. of Royal	5.7	0.4	Nil	36	1.4	3.5	2.6	2.3	29	31	0.01	0.09	83	2	69	7.16
115	N. of Flin Flon	8.2	0.3	Nil	38	1.4	3.0	2.1	4.0	31	32	0.26	0.04	69	1	67	6.33
119	W. of Flin Flon	12	0.4	Nil	46	1.2	2.8	1.5	7.5	38	42	<0.005	0.36	96	7	85	6.15
H	Holt Lake	2.1	0.5	Nil	10	0.4	1.2	1.1	1.8	8	10	0.06	0.04	27	1	26	7.21
T	Tomahawk Lake	3.8	1.7	Nil	15	1.7	2.2	1.9	4.9	14	19	0.02	0.08	55	<1	52	7.43